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LYMAN J. BRIGGS, Director

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[Supersedes Circular C44]

POLARIMETRY, SACCHARIMETRY AND THE SUGARS

By
FREDERICK J. BATES and ASSOCIATES

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PREFACE

This Circular supersedes National Bureau of Standards Circular No. 12, issued July 6, 1906, and Circular No. 44, issued January 15, 1914, and revised November 1, 1917. The main object of this treatise is to explain the application and manipulation of polarized light for industrial, analytical, and theoretical purposes. The principal application of polarized light is embodied in the many modifications of the polariscope. The increasing applications of polarized light to the arts and sciences has led to a proportionate increase in the requests made to the Bureau for information. In this Circular an attempt is made to answer as far as possible such inquiries as well as furnish information of a broader character and in greater detail than could be given by letter. In order to present the necessary explanations, simple physical conceptions and deductions have been used. Such explanations, however, are not to be construed or interpreted as an explanation of the physical theory of optical activity. In spite of the numerous mathematical treatments of this subject in recent years, and in spite of the important contributions to the subject of the structure of naturally optically active compounds from the chemical viewpoint, a satisfactory explanation of the phenomenon which comprehends existing experimental facts is still lacking. The general subjects of magneto and electro optics in relation to polarized light are not discussed, as they do not come within the province of this treatise.

Van't Hoff and Le Bel discovered how to select from substances of known chemical structure those substances which produce an angular rotation of the plane of polarized light. There followed a widespread utilization of the polariscope in the chemical industries and in chemical research. However, despite the voluminous researches which resulted and the fact that physicists have probed deeply into the nature of light in general and polarized light in particular, as well as the nature of the ultimate particles of which all substances are built up, the mechanism of the interaction between polarized light and the structure of optically active substances is still in a state of controversy, as illustrated by the theories of Born, Kuhn, Boys, and others. No attempt therefore has been made to present a picture of the present controversial state of the physical theory of the nature of optical activity. As a justification for the special applications of the polariscope given in this Circular, it may be stated that carbohydrate chemistry, and carbohydrate industry dependent upon carbohydrate chemistry, could hardly have developed to the magnitude it has attained in recent years without the aid and guidance of the polariscope. Conversely, no better insight into the various applications of quantitative measurements with the polariscope can be given than the study of the specific investigations of carbohydrate chemistry. The application of the polariscope in other fields of chemistry, such as essential oils, hydrocarbons, alkaloids, and other optically active substances, will present no difficulties to the chemist familiar with its application in carbohydrate chemistry. Because of this fact, carbohydrate investigations have been given a prominent place in this Circular.

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POLARIMETRY, SACCHARIMETRY, AND THE SUGARS

By Frederick J. Bates and Associates

ABSTRACT

For the purposes of this treatise, the subject matter presented has been divided into five parts. The first of these covers a mathematical treatment of the physical phenomena and a description and discussion of the physical equipment, such as polarimeters, saccharimeters, and accessory apparatus utilized in the study and applications of polarized light.

The development of polarimetric equipment is discussed from the historical standpoint, but emphasis has been placed upon recent developments. This phase of the subject is followed by a general discussion and evaluation of the numerous methods for the analysis and study of raw and refined sugars and sugar products. Special emphasis has been made upon recent contributions and applications of physical science to chemical analysis, including electrical conductivity, colorimetry, refractometry, densimetry, hydrogen-ion concentration, turbidity and viscosity. The latter subject includes the Bureau's recent contributions and important new data on the subject.

The methods of preparation and properties of the sugars and their derivatives are given in considerable detail. In this connection a detailed study of the literature has been made and the most dependable methods of preparation of the more important sugars and their derivatives are given.

A section of general information relating to such subjects as special tests by the Bureau, issuing of standard samples, certificates and statements, test fees, etc., is included.

One hundred and fifty numerical tables are given, which provide a working basis for experimental and analytical purposes. The data given in certain of these tables have not heretofore been available. In table 148, "Optical Rotation and Melting Point of Certain Sugars and Their Derivatives," the data given are the result of a careful examination of a vast literature. There are also included the United States Customs Regulations and a digest of the Proceedings of the International Commission for Uniform Methods of Sugar Analysis.

PART 1. POLARIZED LIGHT, POLARIMETERS, SACCHARIMETERS, AND ACCESSORY APPARATUS

I. INTRODUCTION

Since the organization of the National Bureau of Standards in 1901 there has been submitted for test a great variety of polariscopic apparatus typifying the designs and methods of construction adopted by American and European manufacturers. The Bureau is equipped with examples of the standard apparatus of the leading polariscope builders, as well as special apparatus for work requiring the highest attainable precision. For most of the apparatus sent to the Bureau for test no intimation is given as to the degree of accuracy to be certified. In these cases it is the practice to report the tests to such precision as the Bureau's previous experience with the type of appa-

ratus involved has shown it to merit. On the other hand, a precision is frequently requested which is greater than the apparatus justifies. In general, two grades or standards of accuracy have been found adequate in standardizing polariscopic apparatus. The first grade is for work requiring the highest commercial accuracy. The second grade is for all scientific work except special research in which the precision of the supplementary data entering into the ultimate results justifies a still higher accuracy in the polarimetric data. In the latter case the Bureau will cooperate with investigators in providing not only for tests of the highest precision but also, on request, in furnishing any information at its disposal in reference to methods of measurement and the design and construction of special apparatus. It also is the desire of the Bureau to cooperate with manufacturers, scientists, and others in bringing about more satisfactory conditions relative to the weights, measures, measuring instruments, and physical constants used in polariscopic work, and to place at the disposal of those interested such information relative to these subjects as may be in the Bureau's possession.

II. POLARIZED LIGHT

1. NATURE OF POLARIZED LIGHT

According to the modern wave theory, light is an electromagnetic disturbance that travels as trains of waves oscillating transversely to the direction of propagation. The associated electric and magnetic forces are, therefore, not only perpendicular to each other but also to the direction of advance. Moreover, the oscillations consist, in general, not only of very nearly periodic variations in the magnitudes of the forces but also of more or less periodic changes in the directions of the force vectors about the propagational axis. The variations in magnitude for the two associated forces are generally so simply related that, although they are 90° out of phase, it is customary in most problems related to polarimetry to consider only the variations in one force. Since the electric force is commonly identified with the light vector, its variations are those usually discussed in such problems.

Although the variations in magnitude and direction of this vector are oscillatory in character, they would undoubtedly seem to possess only the slightest indication of their intrinsic periodicity if it were possible actually to see them as they occur in any beam of polychromatic light. Moreover, the amplitude and period continually vary even if the light is practically monochromatic; also even if the component in any direction perpendicular to the propagational axis is segregated in order to eliminate the directional variation in the unresolved oscillation. In comparison to the rapidity of the primary oscillation, however, the variations in amplitude and period develop slowly. For the sake of simplicity, it is customary, therefore, to consider that both amplitude and period are constant for time intervals that are very great compared to the period. In many cases, this makes it possible to treat the complex oscillations of light as very simple forms of periodic motion.

Of the possible oscillatory forms of periodic motion in a wave-like disturbance such as light, the simplest to visualize and the easiest to analyze are the rectilinear, circular, and elliptical. Obviously, the last of these is the most general of the three, since in a broad sense it

includes the others as limiting cases. Whenever the magnitude and direction of the light vector appear to vary continually in accordance with any one of these simple periodic motions, the light is said to be plane, circularly, or elliptically polarized, respectively. If its oscillation appears to conform only partially or not at all to any of these forms, the light is accordingly said to be partially polarized or unpolarized. Under natural conditions light as emitted by an extended source is never completely polarized. Presumably, however, its oscillation is always either approximately plane, circular, or elliptical for very small intervals of time. In that case, the lack of detectable polarization by the use of ordinary polarimetric tests must be the result of the very rapid changes from one form of oscillation to another, and the changes must develop in such a way that all effects of the light are symmetrical about the propagational axis [1, p. 254].[1]

Since the oscillation in plane polarized light is rectilinear, the electric vector in a beam of such light is perpendicular to a fixed plane that lies parallel to the axis pf propagation. This plane is parallel to the magnetic vector and is called the plane of polarization. The angular position of this plane with respect to some chosen reference plane—also parallel to the propagational axis—is the azimuth (γ_P) of the plane of polarization. For example, if a plane polarized beam of parallel light rays is being propagated in the positive Z-direction, and $\gamma_P=0$ with respect to the YZ-plane, the light vector and its oscillations are parallel to the XZ-plane. The oscillation caused by the passage of the wave trains of light at any point, z_0, in such a beam may be visualized as rectilinear oscillations of that point about its rest position (for instance, $x=0$, $y=0$). While the point is thus representing the supposedly continuous, rectilinear, and periodic variation of the light vector, its displacement from rest position at any time, t, may be expressed by the relation

$$x=a \cos (\omega_x t-\alpha). \tag{1a}$$

If the light is polarized so that $\gamma_P=\pi/2$, the oscillation is parallel to the YZ-plane, and the displacement of the point at any time, t, will be

$$y=b \cos (\omega_y t-\beta). \tag{1b}$$

These are the equations of the rectilinear oscillations obtained by resolving the oscillation either of an unpolarized or of a polarized beam into rectangular rectilinear components.

If the light is practically monochromatic, the amplitudes, a and b, will be approximately constant over time intervals that are great compared to the oscillation period, although in general both actually vary many thousands of times a second between zero and successive maxima of different magnitudes. The angular frequencies, ω_x and ω_y, likewise approach constancy over similar comparatively large time intervals, although they actually vary between limits within the spectral range of the "monochromatic" light. Moreover, these frequencies when observed simultaneously are, in general, different even at common points in beams which are components of a single beam.

[1] The numbers in brackets correspond to the numbered literature references given throughout this Circular.

Angular velocities, ω, are related to the period, T, and frequency, ν, by the identities

$$\omega=\frac{2\pi}{T}=\frac{2\pi c}{\lambda'}=2\pi\nu,$$

where c and λ' are the velocity and wave length of the light in vacuum. The "phase angle" constants, α and β, merely signify that at the time, $t=0$, the displacements may not have had their maximum positive values, a and b. As written, they are equivalent, when positive, to lags or retardations.

The phase difference between the wave trains of the two beams, 1_a and 1_b, is $\beta-\alpha=\delta_0$ at z_0 (when $t=0$), and a positive value for this difference indicates that the y-train lags behind the x-train. If $\omega_x=\omega_y$ at all times, this lag obviously remains constant; but in general this is not the case, even when the components come from a common and practically monochromatic source. Consequently, after a time, t, the lag at z_0 becomes

$$\Delta_t=(\omega_y-\omega_x)t-(\beta-\alpha)=\delta_t-\delta_0.$$

However, under the above conditions relative to the source, $\delta_t=(\omega_y-\omega_x)t$ never increases with time indefinitely (as it would if the frequencies or the components were so different that $\omega_y-\omega_x$ was large and always had the same sign); but it may nevertheless vary uncertainly between positive and negative values of uncertain magnitude, because the difference in frequencies, although small, is subject to erratic variations and changes in sign. Only when $\omega_y-\omega_x$ becomes almost vanishingly small at all times will δ_t remain approximately zero.

In polarimetric measurements, the differences in phase between two component trains may be required for other common points (or pairs of related points) along the paths traversed. The expression for the change in the phase difference between two such points is immediately obvious when the equations expressing the displacements for both component beams in terms of both t and z are considered. These equations are

$$\left.\begin{aligned} x&=a\cos\left(\omega_x t-\alpha-2\pi\frac{z_x-z_0}{\lambda_x}\right)\\ y&=b\cos\left(\omega_y t-\beta-2\pi\frac{z_y-z_0}{\lambda_y}\right)\end{aligned}\right\}. \tag{2}$$

From these the expression for the difference in phase between the oscillations at z_y and z_x (points in y- and x-beam, respectively) is at the time, t,

$$\Delta_{(t,z)}=\delta_t-\delta_0-2\pi\left[\frac{z_y-z_x}{\lambda_y}+(z_x-z_0)\left(\frac{1}{\lambda_y}-\frac{1}{\lambda_x}\right)\right].$$

The first terms, δ_t and δ_0, have been discussed and means of making them approach zero will be considered later. A portion, $\delta_d=2\pi(z_y-z_x)/\lambda_y$, of the term in parentheses expresses the phase difference caused when the path lengths, D_1 and D_2, traversed by the beams are differ-

ent. Such differences appear, for example, when light passes through doubly refracting plates and the component beams diverge. (In that case $d=D_1-D_2$). The second portion in the parentheses expresses the phase difference caused by a difference in the wave lengths of the two beams which have traversed equal paths ($D=D_1=D_2$). If $z_x=z_y$, and $z_0=0$, then $\delta_d=0$, and the whole term in parentheses becomes simply $\delta_D=2\pi z(1/\lambda_y-1/\lambda_x)$.
If the difference in wave length is entirely the result of a difference between the refractive indices, μ_y and μ_x, of the medium for the two beams, this phase difference becomes

$$\delta_D=\frac{2\pi z}{\lambda'}(\mu_y-\mu_x), \tag{3}$$

since $\lambda'=\mu_x\lambda_x=\mu_y\lambda_y$ if the component beams have the same wave length in vacuum. That is, δ_D is the phase difference introduced between the two component beams after traversing paths of equal length in a doubly refracting medium. This relation is used in computing the order of thin doubly refracting plates [2, p. 554].

2. INHOMOGENEITY OF LIGHT AND INCOHERENCY OF LIGHT BEAMS

In the foregoing paragraphs it has been stated that the amplitude and frequency of the oscillations, even in so-called monochromatic light, are never constant. Moreover, the variations in these oscillation characteristics are always unlike in any two plane polarized component beams obtained directly from an unpolarized beam. Under these conditions, the component beams are said to be incoherent. That is, in strictly coherent beams, the ratio of the amplitudes of the oscillations at corresponding points in the beam paths must remain constant and the frequencies must remain equal indefinitely. To say the least, the variability of amplitude and frequency in light oscillations is closely related to the inhomogeneity of the light. Two views of this relation may be taken, either inhomogeneity is the cause of the variability or the reverse of this.

That light as perceived is always inhomogeneous is obvious when it is considered that even the narrowest spectral line obtainable actually represents an infinitude of slightly different frequencies, and that inhomogeneity is related to variability of amplitude is suggested by the composition of rectilinear oscillations in the same azimuth which have constant amplitudes and constant but slightly different frequencies, although, as far as light is concerned, such constancy is purely a convenient assumption. If the displacements contributing to the resultant at z_0 and time, t, are

$$x_1=a_1 \cos (\omega_1 t-\alpha_1) \text{ and } x_2=a_2 \cos (\omega_2 t-\alpha_2),$$

the resultant (assuming that the displacements are additive) will be by simple trigonometric operations

$$x=x_1+x_2=A_1 \cos (\omega t-\alpha')-A_2 \sin (\omega t-\alpha')=a \cos (\omega t-\alpha). \tag{4}$$

Chiefly as aids in the performance of these operations and in the interpretation of the results, the following identities may be written

$$A_1=(a_1+a_2)\cos(\omega' t-\alpha'')=a\cos\alpha'''$$
$$A_2=(a_1-a_2)\sin(\omega' t-\alpha'')=-a\sin\alpha'''$$
$$2\omega=\omega_1+\omega_2,\ 2\omega'=\omega_1-\omega_2,\ 2\alpha'=\alpha_1+\alpha_2$$
$$2\alpha''=\alpha_1-\alpha_2$$
$$a^2=A_1^2+A_2^2=a_1^2+a_2^2+2a_1a_2\cos 2(\omega' t-\alpha'')$$
$$\alpha=\alpha'+\alpha''',\ \tan\psi=\frac{a_2}{a_1}$$
$$\tan\alpha'''=-\frac{A_2}{A_1}=-\tan\left(\frac{\pi}{4}-\psi\right)\tan(\omega' t-\alpha'').$$

From this it is clear that the amplitudes, A_1 and A_2, are periodic functions of the time, and that consequently the amplitude a is also. The frequency of this variation is, however, comparatively small, since ω is much greater than ω'. Although ω is constant, the variability of α is really the equivalent of a variable frequency in the resultant. This simple example indicates, therefore, that both amplitude and frequency of an oscillation, which is the resultant of an infinitude of homogeneous elementary wave trains with slightly different frequencies, must be variable. At least this must be the conclusion if it is permissible to assume that any such large number of elementary trains as is required to produce a spectral line can be divided into two parts which yield unrelated resultants with slightly different frequencies that approximate those of the components in the above example. Thus if by any chance or because of any reason these partial resultants possessed amplitudes and frequencies that varied little during intervals equivalent to many thousand periods of the elementary trains, their resultant would nevertheless possess all of the frequency and amplitude variations shown during a similar interval by the above simple example of a resultant. Moreover, this conclusion applies to the two partial resultants themselves after due consideration is given to the probable condition that the differences between the frequencies of their components (partial resultants restricted to still smaller spectral ranges) would presumably be smaller.

If, in the case of rectangular components, it is further assumed that the number, amplitudes, and phases of the elementary trains contributing to the y- and to the x-resultant oscillations are different, it is obvious that there will be no relationship between the variabilities appearing in either the amplitudes or the frequencies of the two resultants. Hence, rectangular component beams obtained from an unpolarized beam will not be coherent, if they are resultants of that nature.

If the oscillations of the elementary trains contributing to the resultants were to have constant and equal amplitudes and frequencies, so that the resultant amplitudes and frequencies would be constant, as earlier assumed, it would follow that such trains must remain unbroken and unchanged for time intervals at least as long as the intensity of the resultant light beam appears to be unvarying. Such a condition is undoubtedly contrary to that which actually exists, since the innumerable oscillators that originally contribute the elementary trains from a radiant and so-called monochromatic source are, compared to the time required to obtain a simple polarimetric observation, extremely short-lived, even though each may oscillate many thousand times. Consequently, during each oscillation period of the resultant, the contributions from a small portion of the oscillators cease and are

replaced by others from freshly excited oscillators. In general, the number, oscillation forms, phases, and to some extent the frequencies of the replacements during a period, will differ from those of the replaced contributions, although between averages taken over long time-intervals these differences are not apparent. Moreover, the contribution from each oscillator may change its oscillation form, etc., more or less gradually throughout the time interval in which it emits.

In response to these variations in the number of contributing oscillators and in the oscillation form, etc., of the contributions, the resultant at any point in a light beam continually and compatibly alters its oscillation characteristics, regardless of the manner in which the contributions arrive at that point from the source. That is, even in light from the nearest possible approach to a monochromatic source, the resultant oscillation will vary in a random manner through all elliptical forms from rectilinear to circular without favor, and the direction of the light vector at its maximum during each oscillation will vary from period to period without favoring any azimuth. Moreover, the maximum magnitude of the vector during a period may on occasion approach zero if the amplitudes and phases of the elementary trains are such that almost complete interference occurs in some segments of the resultant train. Consequently, both the amplitude and frequency of any rectilinear component obtained from the resultant will also vary continually in a random manner approaching that previously suggested, and these variations in rectilinear components (taken at right angles, for instance) will be unlike. That is, such components of natural light are ordinarily incoherent.

That this incoherence must exist is perhaps clearer when it is considered that in general an oscillator contributes unequally to the components and that this inequality varies with the oscillator. Only when a rectilinear component of unpolarized light is further resolved into two or more rectilinear (or elliptical) components does each oscillator distribute its contribution coherently between the components and also in the same relative degree (as the other oscillators) to any one component. Therefore, such secondary components are coherent as a result of artificial manipulation.

The oscillation changes, contributed to a resultant by such an infinitude of oscillators with almost identical frequencies, develop quite slowly in comparison with the rapidity of primary oscillation. This comparative slowness results because the changes in the characteristics of the emission of an individual oscillator develop gradually and also because the number of replacements per period of the primary oscillation is small when compared to the very great number of simultaneously contributing oscillators. It is obvious, however, that on the average every one of this great number will be replaced within the lifetime of the youngest. Consequently, if one of a pair of secondary, coherent components that are plane polarized in different azimuths suffers a relative retardation corresponding to this time interval by being made to pass over a path sufficiently longer than that traversed by the other, the coherency of the two components will then no longer be evident, and the resultant light on their recombination will be unpolarized.

The effect of this incoherency appears not only in polarized light but also in the interference phenomenon of common light. That is, two incoherent beams (for example, beams from different parts of

some source) do not produce observable (so-called destructive) interference. Likewise, observable interference is never obtained when two primary plane polarized components of an unpolarized beam are brought into the same azimuth and recombined. This is the case even without introducing any path difference which would cause incoherence. Interference effects between unpolarized components, such as are produced from an unpolarized beam by an interferometer, occur because the component oscillations in any azimuth and in either component beam has its counterpart in the same azimuth in the other. Presumably, it will be only when the relative retardation between such beams becomes approximately equivalent to the lifetime of an oscillator that all observable interference vanishes. By using light from a suitable spectral-line source, interference effects have been observed until the difference in path exceeded a million wave lengths. This difference is of the order of 50 cm in air and corresponds roughly to a time interval of one 600 millionth of a second. Polarimetric measurements, however, are seldom concerned with retardations which exceed a few wave lengths.

3. COMPOSITION OF RECTILINEAR OSCILLATIONS HAVING DIFFERENT AZIMUTHS

The superposition of two coherent plane polarized beams not having the same azimuth yields, in general, elliptically polarized light; or if they are not coherent, unpolarized light. Ordinarily it is necessary to consider only such beams as are polarized at right angles. Equations 1a and 1b are representative of the component oscillations occurring at any common point, z, in these beams. That is,

$$x=a \cos (\omega_x t-\alpha) \text{ and } y=b \cos (\omega_y t-\beta).$$

If the conditions that b/a, ω_x, and ω_y are constant and that $\omega_x-\omega_y=0$ are approximated to a sufficient degree, the oscillations are coherent; otherwise, they are not. For the moment it will be considered that the coherency of the beams is a matter of doubt.

Assuming that resultant vector, r, of these oscillations is obtained in the same manner as the resultant in the composition of forces at right angles, it follows that

$$r^2=x^2+y^2=a^2 \cos^2 (\omega_x t-\alpha)+b^2 \cos^2 (\omega_y t-\beta).$$

By writing the identities (for comparison, see equation 4).

$$\left.\begin{array}{ll} \text{(a)} & \omega_x=\omega+\omega',\ \omega_y=\omega-\omega' \\ \text{(b)} & \alpha=\Delta'-\Delta,\ \beta=\Delta'+\Delta \\ \text{(c)} & \delta=\omega' t+\Delta \\ \text{(d)} & a^2+b^2=A^2+B^2 \\ \text{(e)} & (a^2+b^2) \cos 2\delta=(A^2-B^2) \cos 2\delta' \\ \text{(f)} & (a^2-b^2) \sin 2\delta=(A^2-B^2) \sin 2\delta', \end{array}\right\} \quad (5)$$

and then by performing the necessary simple trigonometric transformations, it develops that

$$\left.\begin{array}{l} r^2=a^2 \cos^2 (\omega t-\Delta'+\delta)+b^2 \cos^2 (\omega t-\Delta'-\delta) \\ \quad =B^2+(A^2-B^2) \cos^2 (\omega t-\Delta'+\delta') \end{array}\right\} \quad (6)$$

If the conditions for coherence are strictly met, $\Delta'-\delta'$ is constant and eq 6 is the equation of an ellipse, of which A and B are the semiaxes. Furthermore, the magnitudes of the amplitudes, a and b, lie between those of the semiaxes. Consequently, the identity

$$\frac{a^2-b^2}{A^2-B^2}=\cos 2\gamma \tag{7}$$

may be written, and it develops later that γ and $\gamma\pm\pi/2$ are the azimuths of the semiaxes.

If the conditions for coherence are almost met but not to the degree essential in elliptically polarized light, A, B, δ, ω, and γ are then all functions of t, and B/A and γ vary between 0 and ∞ and between 0 and 2π, respectively. The resultant light is unpolarized in this case, and an indicator point tracing out the variations in the magnitude and direction of the vector, r, would describe a long succession of unrepeated patterns akin to a complicated series of almost elliptical Lissajous figures, in which no ratio of axes or azimuth of major dimension is favored. Moreover, the possibility that both the major and minor dimensions occasionally approach zero almost simultaneously cannot be excluded.

A similar pattern intended to represent the vector oscillations in white light is too complicated and irregular for the imagination. However, even in the case of a component, as obtained from a beam of white light by an interferometer, every infinitesimal portion of its spectrum is practically coherent with the same elementary spectral portion of the other component. (This is true provided the previously mentioned limitation as to the relative phase (path) difference is imposed.) Consequently, the so-called channeled spectra appear whenever white light is analyzed by a spectroscope after it has been passed through an interferometer. Analogously, two rectangular components of a plane polarized beam of white light, which are recombined after one has been subjected to a relative retardation of several wave lengths that increases with decreasing wave length, will yield a spectrum in which every spectral element is, in the general sense, elliptically polarized. That is, as the wave length decreases, the oscillation forms will pass again and again through a series ranging from rectilinear through all degrees of elliptic to circular polarization. Moreover, on passing through the circular form, the azimuth of the major axis will shift from the first to the second quadrant or in the reverse direction. Such a resultant on being passed through a properly oriented nicol will, when examined with a spectroscope, also yield a channeled spectrum.

Light from a so-called monochromatic source emitting a line of average breadth (although the narrowest possible line still encompasses an infinitude of infinitesimal spectral elements), presents no appreciable spread in oscillation form after being treated as suggested above in the discussion on white light. That is, the resultant vector oscillation, even when representing all frequencies in the line, very closely approximates a simple elliptical form. As time proceeds, however, the ratio of the axes and their azimuths will fluctuate slightly about average values and the major axis will occasionally approach zero. After a sufficiently large number of periods, the representative pattern

of this oscillation is consequently an elliptical disk (if such a representation may be allowed) which through variations in the denisty of its shading could be made to suggest the dimensions of the approximate ellipses occurring most frequently. Regardless of these variations, the individual ellipses, representing the resultant oscillations of practically coherent perpendicular components, are all so nearly closed and have so nearly the same form and azimuth that the deviations from a perfectly stable oscillation form are negligible as far as all ordinary problems of elliptically polarized light are concerned.

For practical purposes, therefore, it may be considered that $2\omega'=\omega_x-\omega_y=0$, and consequently that $2\delta=\beta-\alpha=2\Delta$. It also may be assumed that γ and the ratios $b/a=\tan\psi$ and $B/A=\tan\Psi$, are constants, although a, b, B, and A vary. (As a matter of convenience, it will be considered that the functions representing these ratios are always positive.)

From the identities (d), (e), and (f) in eq 5 it is evident that

$$\left.\begin{array}{l}(A^2-B^2)^2=a^4+b^4+2a^2b^2\cos 4\delta\\ (a^2+b^2)\tan 2\delta'=(a^2-b^2)\tan 2\delta\\ a^2b^2\sin^2 2\delta=A^2B^2 \text{ or } \sin 2\delta=\pm AB/ab\end{array}\right\}. \tag{8}$$

The double sign in the last relation will ordinarily be neglected, since it merely shows that $\sin 2\delta$ may be either positive or negative. It can be shown by graphic methods, however, that the vector rotation is positive (counter-clockwise to one looking toward the source, or, that is, in the negative direction) or negative according as this sine is positive or negative. Moreover, it can be shown that the major axis lies in the first and third quadrants or in the second and fourth, according as the $\cos 2\delta$ is positive or negative. With respect to the position of the major axis it also appears from identity 7 that γ lies between $\pi/4$ and $3\pi/4$ or between $-\pi/4$ and $+\pi/4$, according as $a\lesseqgtr b$.

On proceeding further with the development of the relationships existing between the identities used in the previous pages, it may be shown that

$$\left.\begin{array}{ll}\text{(a)*} & \sin 2\delta\sin 2\psi=\sin 2\Psi\\ \text{(b)} & \tan 2\delta'=\cos 2\psi\tan 2\delta\\ \text{(c)*} & \cos 2\psi=\cos 2\gamma\cos 2\Psi\\ \text{(d)} & \sin 2\delta'=\sin 2\delta\cos 2\gamma\\ \text{(e)*} & \cos 2\delta=\dfrac{\tan 2\gamma}{\tan 2\psi}=\dfrac{\sin 2\gamma\cos 2\Psi}{\sin 2\psi}=\cos 2\delta'\cos 2\Psi\\ \text{(f)} & \cos 2\delta'=\dfrac{\sin 2\gamma}{\sin 2\psi}\\ \text{(g)} & \sin 2\gamma=1/2[\sin 2(\psi+\delta')+\sin 2(\psi-\delta')]\\ \text{(h)*} & \tan 2\delta=\dfrac{\tan 2\Psi}{\sin 2\gamma}.\end{array}\right\}. \tag{9}$$

Asterisks indicate those equations found in the Theory of Optics [4, p. 15]. However, it will be noted that Schuster used the identity $\delta=\beta-\alpha$, as in the discussion of eq 1a and 1b.

Certain of these relationsips are required in all measurements on elliptically polarized light, and it will be noted that after any two of

the angles have been determined experimentally, the remaining four may, in general, be computed.

In order to appreciate that γ is the azimuth of the major axis, it will be noted that $\omega t-\Delta'+\delta'=0$ when $r^2=A^2$, and that $(y/x)_{r_2=A_2}$ is the tangent of the azimuth of the axis A with respect to axis X. It then can be shown by the use of the previously developed relations that

$$\tan\gamma=\frac{b\cos(\delta+\delta')}{a\cos(\delta-\delta')}. \tag{10a}$$

Likewise, when $r^2=B^2$,

$$\tan\gamma_B=\left(\frac{y}{x}\right)_{r^2=B^2}=\frac{b}{a}\frac{\sin(\delta'+\delta)}{\sin(\delta'-\delta)}=\cot\gamma,$$

where γ_B is the azimuth of B, also measured from the X-axis.

The direction of the rotation of the vector, r, may also be found from the change in its azimuth γ_r with time. Thus

$$\tan\gamma_r=\frac{y}{x}=\frac{b}{a}\frac{\cos(\omega t-\beta)}{\cos(\omega t-\alpha)} \tag{10b}$$

$$\frac{d\gamma_r}{dt}=\frac{b}{a}\frac{\omega\cos^2\gamma_r}{\cos^2(\omega t-\alpha)}\sin 2\delta$$

or, as previously stated, the sign of the sine of the relative retardation determines the direction of the vector rotation when a and b are considered as always being positive.

From eq 10a, 10b, and (a), (b), and (f) of eq 9 it is evident that $\gamma=\psi$, $B=0$, $\delta'=0$, and $\Delta'-\delta'=\alpha=\beta$, if $\delta=0$. That is, the light is plane polarized, and the direction of its oscillation lies in the first and third quadrants. Many other special cases, where $0<b/a<\infty$ and δ has positive or negative values of various multiples of $\pi/4$, may be analyzed easily by means of eq 5 to 10b.

4. COMPOSITION OF CIRCULAR OSCILLATIONS

If beams of really homogeneous light were obtainable, they would, in the general sense, always be elliptically polarized, and if their periods were identical, their resultant would also be elliptically polarized in the broader sense. Within limits, the same is true in the case of elliptically polarized and practically homogeneous real light as long as the beams are coherent. Any beam of plane polarized light may, as a matter of fact, be considered as the resultant of two or more coherent beams of elliptically polarized light. However, it ordinarily is necessary to consider only that case in which the components of an elliptically or plane polarized resultant are two in number, and it will be assumed now that the components are circularly polarized. [3, p. 443].

As shown by eq 6, representative oscillations of two such components may be defined by their vectors, r_1 and r_2, and the continually and uniformly changing vector azimuths $\gamma_1=\pm(\omega t-\alpha_1)$ and $\gamma_2=\pm(\omega t-\alpha_2)$ where the double signs indicate that the rotations may be either positive or negative. The identities $\gamma_1=\gamma'+\gamma''$ and $\gamma_2=\gamma'-\gamma''$ are used to facilitate the following transformations. It will be noted that γ' is the mean azimuth of the two vectors, while $2\gamma''$ is

the angle between them. Assuming again that the resultant vector is found as in the composition of forces, it follows that

$$r^2=r_1^2+r_2^2+2r_1r_2 \cos 2\gamma'' \tag{11}$$

and that

$$\tan \gamma=\frac{r_1 \sin \gamma_1+r_2 \sin \gamma_2}{r_1 \cos \gamma_1+r_2 \cos \gamma_2},$$

where γ is the azimuth of the resultant. By writing the additional identities

$$\tan \psi=\frac{r_2}{r_1} \text{ and } \gamma=\gamma'+\gamma''',$$

it will be found that

$$\tan \gamma'''=\frac{r_1-r_2}{r_1+r_2} \tan \gamma''=\tan (\pi/4-\psi) \tan \gamma''.$$

This angle, γ''', lies between the resultant and the mean azimuth of the component vectors and obviously becomes zero whenever $r_1=r_2$ or $\gamma''=0$.

Since the component vectors may rotate in the same or opposite directions, it becomes necessary to consider the two cases. If they rotate in the same direction, $\gamma'=\pm\left(\omega t-\frac{\alpha_1+\alpha_2}{2}\right)$ and $\gamma''=\frac{\alpha_1-\alpha_2}{2}$. Consequently, the resultant and its direction are $r^2=r_1^2+r_2^2+2r_1r_2 \cos (\alpha_2-\alpha_1)$ and $\gamma=\pm\left(\omega t-\frac{\alpha_2+\alpha_1}{2}\pm\gamma'''\right)$. Under these conditions, the resultant light is always circularly polarized.

If the component vectors rotate in opposite directions, $\gamma'=\frac{\alpha_2-\alpha_1}{2}$ and $\gamma''=\pm\left(\omega t-\frac{\alpha_2+\alpha_1}{2}\right)$. Moreover, by substituting A^2+B^2 and A^2-B^2 for $2(r_1^2+r_2^2)$ and $4r_1 r_2$ and using eq 11, the resultant and its azimuth are given by the expressions $r^2=B^2+(A^2-B^2) \cos^2 \left(\omega t-\frac{\alpha_1+\alpha_2}{2}\right)$ (see eq 6) and $\gamma=\frac{\alpha_2-\alpha_1}{2}\pm\gamma'''$, where γ''' is the azimuth of the resultant with respect to the major (or minor) axis of an ellipse representing the variations in r. Under such conditions, the resultant light is always elliptically polarized if $r_1\neq r_2$. Moreover, the azimuth of the major axis is that of vector r when $\omega t=(\alpha_1+\alpha_2)/2$ or, what is the same, when γ'' (and, consequently, γ''' also) becomes zero. The azimuth, γ_A, of the major axis is therefore $(\alpha_2-\alpha_1)/2$.

If the component vectors not only rotate in opposite directions but also are equal ($r_1=r_2$), it is apparent that $B=0$ and $\gamma'''=0$. Therefore, $r=A \cos \left(\omega t-\frac{\alpha_1+\alpha_2}{2}\right)$ and $\gamma=\frac{\alpha_2-\alpha_1}{2}$ That is, in the composition of circular components with different directions of rotation, the resultant light is plane polarized in an azimuth determined alone by the phase difference between the components. The roles played by the differences in amplitude and phase are, therefore, the reverse of those played by the same differences in the composition of rectilinear components.

5. POLARIZATION BY DOUBLE REFRACTION

As already stated, natural light may be considered as being the resultant of two or more incoherent component beams of light that are plane polarized in different azimuths. Moreover, when the light is actually resolved into components they are also found to be incoherent, and, if their planes of polarization are not exactly brought into a common azimuth, their recombination again results in unpolarized or partially polarized light. However, polarized light can be obtained from natural light by resolving it into plane polarized components and then rotating the polarization planes to a common azimuth before the components are recombined, by diverting the components into individual paths which are so divergent that recombination does not occur, or by employing some other means, such as the nicol prism, which eliminates all but one plane polarized component. Plane polarized light is easily produced by any of these methods, but circularly and elliptically polarized light are not usually obtained so directly from natural (unpolarized) light.

In general, the resolution of unpolarized (also of polarized) light into two polarized component beams occurs naturally whenever a beam of light traverses any doubly refracting (anisotropic) crystal. That is, a beam of light on entering such a crystal is resolved into two differently refracted beams, which on emergence are slightly separated and, ordinarily, plane polarized at right angles, except when they parallel certain unique directions in the crystals. The difference in the refraction for the two polarized component beams is, in certain selected directions in a number of crystalline minerals, large enough to cause a divergence of the beams that is sufficient to allow the complete elimination of one beam to be accomplished in various ways.

If the incident light is circularly polarized or unpolarized, the differently refracted component beams are of equal intensity; but if it is plane or elliptically polarized their relative intensity varies as the crystal is rotated about the beam as an axis. If plane polarized light is normally incident on a crystal face, the component beams (transmitted by a calcite crystal, for example) are equal in intensity only when the plane containing both refracted beams has an azimuth $\gamma=\psi=\pi/4$ with respect to the oscillation direction of the incident light. The ratio of the intensities for any azimuth is that of the squared sine and cosine of that angle or, if the amplitude of the incident light is a, the corresponding amplitudes of the components are $a \sin \gamma$ and $a \cos \gamma$.

Well-known examples of doubly refracting crystals are tourmaline, calcite, and quartz. These examples belong to the hexagonal (or the trigonal according to some classifications) system and to the class of uniaxial minerals, a class which also includes crystals of the tetragonal system. In optical terminology, quartz crystals are "positive" (or optically prolate) [4, p. 168]. Tourmaline and calcite are both "negative" (optically oblate). These terms are concerned with the relative velocities with which the component beams traverse the crystals in various directions. The wave surface (any surface or surfaces of equal phase) about a point source of light in an isotropic medium is spherical, since there is but one velocity regardless of direction. In a doubly refracting crystal, however, there are two concentric wave

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surfaces and, in uniaxial crystals, one is always spherical while the other is spheroidal. The component beam corresponding to the spherical wave surface traverses the crystal with the same velocity regardless of the path direction, and on entering (or leaving) the crystal obeys the normal laws of refraction. The velocity of the other component beam, as indicated by the spheroid, varies with the direction of the path. In general, a refracted beam corresponding to the spheroid does not lie in the plane containing both the incident beam and the normal to the surface of incidence. The two differently refracted component beams are therefore named, respectively, the ordinary and extraordinary, and, in optically prolate (positive) crystals, the velocity of the former is greater (index of refraction is less) than that of the latter beam, while in optically oblate (negative) crystals the reverse is true. That is, in optically positive crystals, the prolate spheroid representing the wave surface for extraordinary beams lies within the sphere representing a wave surface with the same phase for ordinary beams. In the case of a positive uniaxial crystal, the spheroid and sphere may be conceived of as having been generated by rotating an ellipse and its circumscribing circle about their common diameter, the direction of the major axis of the former. In a negative uniaxial crystal, the oblate spheroid encloses the sphere, and the axis of rotation of the generating ellipse and circumscribed circle is again the common diameter to both, but the direction of the minor axis of the ellipse. In both cases the direction of this common diameter is that of the optic axis and of the vertical crystallographic axis (*C*-axis) of the crystals.

If the wave surfaces for a uniaxial crystal are actually tangent at the points of intersection with their axis of rotation, two component beams traversing the crystal parallel to this axis will possess identical velocities, obey the ordinary laws of refraction, and will not diverge. Consequently, an incident beam of parallel light (polarized or unpolarized) will, after traversing a plate of such a crystal parallel to its optic axis, be unchanged in its polarization characteristics. In all other directions through the crystal the velocities are different, and the component beams are plane polarized at right angles and diverge.

Certain uniaxial crystals (for example, quartz) rotate the plane of polarization (or major and minor axes) when they are traversed parallel to their optic axis by a beam which at incidence is plane (or elliptically) polarized. This has been interpreted as showing that light, traversing these crystals even in a direction parallel to their optic axes, is resolved into components which have slightly different velocities and that sphere and spheroid do not touch [5, p. 580] at their intersections with the mutual axis of generation. It has been shown, moreover, that these components are circularly polarized; or, if the waves travel obliquely to the optic axis, the component beams are elliptically polarized.

The wave surfaces of a uniaxial crystal are a special case of a fourth-degree surface, which is represented analytically by the expression $(x^2+y^2+z^2)(a^2x^2+b^2y^2+c^2z^2)-a^2(b^2+c^2)\ x^2-b^2\ (c^2+a^2)\ y^2-c^2\ (a^2+b^2)\ z^2+a^2b^2c^2=0$, in which it may be assumed that $a \geqslant b \geqslant c$ [3, p. 335]. Obviously, if these constants are equal, the expression reduces to that for the single spherical wave surface of an isotropic medium (noncrystalline materials and also many crystals of the cubic system). If $b=c$ only, the surface becomes a sphere within an oblate ellipsoid; or,

if $b=a$ only, it is a prolate ellipsoid within a sphere. These special cases apply to the so-called "negative" and "positive" uniaxial crystals, respectively. If there is no equality between the constants, neither surface is spherical, and they represent the wave surfaces of biaxial crystals. The three sections of these surfaces by the three principal oscillation planes (XY, YZ, and XZ), obtained by letting z, x, and y, respectively, equal zero, are correspondingly a circle lying within, without, and neither wholly within nor wholly without an ellipse. In the last case the circle obviously cuts the ellipse at four points. The diameters joining opposite intersections give the directions of the axes of single-ray velocity, which make only a small angle with the two respective optic axes of the crystal. The angles between these diameters and also those between the optic axes (axes of single-wave velocity) are bisected by the coordinate directions, X and Z. These bisectors are termed the "acute" and "obtuse bisectrices," according as the bisected angles are acute or obtuse. The crystal is said to be optically negative when X, and positive when Z, is the acute bisectrix. The XZ-plane, since it contains the optic axes, is known as the optic plane, and the Y-direction as the optic normal, of biaxial crystals. In the case of uniaxial crystals it may be considered that the optic axes and acute bisectrix coincide and result in a single optic axis. Consequently, these crystals have no definite optic plane, and the positions of the perpendicular obtuse bisectrix and optic normal about the optic axis are indeterminate.

In uniaxial crystals the optic axis coincides with the crystallographic C-axis (the so-called vertical axis), but in biaxial crystals neither of the optic axes coincides with a crystallographic axis nor, in general, do the coordinate or oscillation axes, X, Y, and Z. That is, in the orthorhombic system, the three mutually rectangular crystallographic axes, A, B, and C, coincide with the oscillation axes, although the disposition of the coincidences varies with the crystal; in the monoclinic system one of the oscillation axes (either X, Y, or Z) coincides with the orthodiagonal axis, B, and the other two without a coincidence lie in the plane of the mutually oblique A- and C-axes; while in the triclinic system an oscillation axis seldom actually, or even approximately, coincides with one of the crystallographic axes, which are all mutually oblique.

As a generalization for both uniaxial and biaxial crystals, it may be stated that when a light beam traverses them along either the X-, Y-, or Z-axis (except the optic axis in uniaxial crystals) it is resolved into two undiverging unequally retarded plane or eliptically polarized rectangular component beams, and that ordinarily the beam, when traversing them in any other direction (except those of the optic and single-ray axes in biaxial crystals), is similarly resolved, except that the components diverge. In uniaxial crystals, however, one component always follows the ordinary laws of refraction, while in biaxial crystals neither of the component beams necessarily does so.

With regard to the above indicated exceptions, a beam paralleling the optic axis is in some uniaxial crystals resolved into two unequally retarded circularly polarized components, while the optic and single-ray axes of biaxial crystals are directions associated, respectively, with internal and external conical refraction. Also, some uniaxial (and possibly some biaxial) crystals resolve nonaxial beams into eliptically rather than plane polarized components.

6. ROTATION OF THE PLANE OF POLARIZATION—PHOTOGYRIC EFFECTS

Most isotropic substances are "optically inactive," or agyric; that is, they do not normally rotate the plane of polarization when transmitting polarized light [4, p. 272]. However, a large number of substances are photogyric. Possibly a preponderance of the crystalline materials might also be included in the class of optically inactive substances, but such a statement cannot be made definitely because too often rotatory power of a crystallogyric material is masked by ordinary double-refraction effects. In the many substances which change the azimuth of the plane of polarization, the rotation is proportional to the length of the light path within them. Under certain influences, all substances may possess a rotatory power.

Substances naturally photogyric are said to be "optically active." Sugar solutions and essential oils are examples of isotropic substances which are photogyric. Some of these substances are known to retain the rotatory power in the amorphous solid state (sugar, tartaric acid, etc.) and also in the vapor state (turpentine oil, etc.). Quartz and cinnabar are well-known examples of crystallogyric substances, and the first of these is exceptionally important because of its extended use in polarimetric and other optical instruments. Even in the isometric, or cubic, system many crystals possess a weak rotatory power. Crystalline sodium chlorate is an example of these, and its rotatory power is the same without regard to the direction of the light path through it. Moreover, in spite of the masking effects of ordinary double refraction, it has been possible of late to show that some of the biaxial crystals also possess a rotatory power. Finally, all substances are magnetogyric, since they rotate the plane of polarization when they are placed in a magnetic field, and when the light path through them has a component parallel to the lines of magnetic force, the effect is that of ordinary double refraction. In this respect an ordinary medium in a magnetic field is somewhat similar to a uniaxial crystallogyric mineral.

Photogyric isotropic substances are isogyric, since they have the same rotatory power, independent of the direction of the light path through them, while many minerals, such as quartz, are anisogyric, since they appear to be "optically inactive" if the path direction is normal to the optic axis, although they rotate the plane of polarization if the path parallels that axis. These minerals are generally known to exist in two crystallographic forms, one of which is dextrogyrate and the other laevogyrate. These forms are also often referred to by other terms, such as "dextrorotatory," "right-handed," and "positive" crystals, in the first case, and by corresponding terms in the second. The two forms often can be distinguished by casual inspection, and in quartz, for instance, the form may be indicated by the oblique striations on certain surfaces if the natural faces are reasonably intact [5, p. 571]. These striations show that the crystals are plagihedral, and if the striations lean to the right when they face the observer and if the apex of the adjacent pyramid is upward, the crystal is dextrogyrate [6, p. 31].

A dextrogyrate substance rotates the plane of polarization in a clockwise direction to an observer looking in the apparent direction of the source and at the clock face. That is, according to the previ-

ously chosen convention, it produces a negative rotation, although in connection with these photogyric effects it is usually called a positive one. Obviously, the direction of the rotation produced by a laevogyrate material is the reverse. Reversing the direction in which light traverses these media does not alter the direction of the rotation. For this reason the rotatory effect is nullified if the light is reflected backward over its path through a naturally rotatory material. In this respect, magnetogyratory effects are different, since these rotatory effects are doubled when the light is returned by reflection over its path through a material situated in a magnetic field of unchanged direction. In other words, if the direction of the light is unchanged and the magnetic field is reversed, the direction of the rotation is also reversed. Consequently, the direction of the magnetorotation in a material must be defined with respect to the direction of the magnetic field and not with respect to that in which the light travels. If the light, in traversing a material in a magnetic field, passes from the south-seeking to the north-seeking pole of the magnet producing the field, the magnetogyric effects, especially in most diamagnetic materials, are usually dextrogyrate according to the photogyric convention. In other words, the effect is apparently more often than not dextrogyrate whenever the light travels opposite to the direction of the magnetic force. From this it appears that the direction of the magnetorotatory effect in diamagnetic substances (for example, glass) is usually that of the amperian current, which would produce the causative magnetic field if a solenoid about the light beam were used instead of a magnet. Dextrogyric and laevogyric effects (defined with respect to the magnetic field) are found, however, in both diamagnetic and paramagnetic media.

In all of these photogyric effects the rotatory power of the medium depends on the wave-length of the light. Usually the rotation in the visible spectrum increases with decreasing wave length, but there are many exceptions, and some media are laevogyric in one part of the spectrum and dextrogyric in another. This change may occur suddenly in the range of an absorption band or gradually in the region between two such bands.

7. CIRCULARLY POLARIZED COMPONENT BEAMS IN PHOTOGYRIC EFFECTS

It has been shown experimentally that plane polarized light, normally incident on a plate of quartz cut perpendicular to the optic axis, is resolved into two equally intense circularly polarized component beams which are transmitted at slightly different velocities and have opposite vector rotations. For paths in directions between the optic axis and its normal, it has also been found that a plane polarized beam is resolved into two elliptically polarized components having different velocities. However, the axis ratios of the elliptical oscillations decrease very rapidly as the direction of the path departs from the optic axis.

Whenever plane polarized light, on entering a naturally or artificially photogyric material, is resolved into two equally intense circularly polarized beams having opposite vector rotations and different velocities in the material, it is obvious that at that instant the amplitudes of the oscillations are equal, ($r_1 = r_2$), and the difference

in phase must be zero. As a consequence, the azimuths of the radius vectors with respect to the original plane of polarization are equal and opposite. When the light emerges from an "optically active" transparent plate, the amplitudes, only slightly changed, are again at least practically equal, but the difference in the velocities of the two component beams while in the plate has now introduced a relative difference in phase (δ_D) which, since there is no appreciable divergence effect, is proportional to the plate thickness, D. Consequently, the light, on the recombination of the circularly polarized components, is plane polarized at an azimuth

$$\gamma=\delta_D=\frac{\alpha_2-\alpha_1}{2}$$

with respect to the plane of polarization of the incident beams; or γ is the change in azimuth of the emergent oscillation plane with respect to incident oscillation plane.

If the subscripts 1 and 2 represent, respectively, counterclockwise and clockwise oscillations, it is apparent (since α_1 and α_2 by convention represent positive retardations) that γ represents a clockwise rotation of the oscillation plane (and also of the plane of polarization) whenever the component, circularly polarized in the clockwise sense, has the greater velocity while passing through the plate; that is, γ is negative, since $\alpha_1>\alpha_2$. This is in accord with the experimental results, which show that the magnetorotation in glass is right-handed (direction of amperian current) and that the clockwise oscillation is actually as well as relatively accelerated by the magnetic field.

Some photogyric absorbing media absorb the circularly polarized component beams differentially, and as a result the amplitudes on emergence are unequal ($r_1\neq r_2$). In such cases the recombined components produce an elliptically polarized resultant, as previously shown. This effect is usually designated as "circular dichroism."

8. POLARIZATION OF LIGHT BY REFLECTION

A specular surface on any transparent material (for example, glass and water) reflects light that at one angle of incidence is almost perfectly plane polarized in the plane of incidence. As discovered by Brewster, this occurs whenever the angle of incidence, θ, is such that $\tan\theta=\mu$ (the refractive index of the material). Since μ varies with the light frequency, the polarizing angle of incidence also varies accordingly. For the best results in obtaining plane polarized light by this method, a monochromatic beam of parallel light rays and a good plane reflector are required. Even then surface films and other imperfections in the reflecting surface (which may be wholly invisible) often cause some incompleteness in the polarization. If the incident light is plane polarized and its plane of polarization and that of incidence are oblique, surface films cause the reflected light to be elliptically polarized to a very slight degree (that is, $\tan\Psi$ is small).

This method of obtaining plane polarized light is very inefficient because only a small percentage of the incident light is reflected. To increase the efficiency, a pile of plates (several transparent plate reflectors in series) is used, but the results are still far inferior to those obtained with other devices. Moreover, the deflection of the re-

flected beam causes so much inconvenience that this method is usually employed only in demonstrational and a few other non-precision instruments.

Regardless of the angle of incidence or number of plates employed, the transmitted beam is never more than partially polarized if the incident beam is unpolarized. Although undeflected, the transmitted beam is, therefore, even less desirable than the reflected one as a source of polarized light.

At all oblique angles of incidence other than the polarizing angle, the reflected, as well as the transmitted, beam is only partially polarized, while at perpendicular and parallel incidence there are no polarizing effects. This naturally suggests that the components of the incident oscillations taken parallel to and perpendicular to the plane of incidence are reflected according to different laws. Such a difference is provided for by the Fresnel equations [3, p. 351], which express the ratios of the reflected amplitudes, a'' and b'', to the incident, a and b, (X- and Y-direction respectively parallel to and perpendicular to the plane of incidence) in terms of functions of the angles of incidence, θ, and refraction, θ'. That is,

$$\frac{a''}{a}=\frac{\tan\,(\theta'-\theta)}{\tan\,(\theta'+\theta)} \text{ and } \frac{b''}{b}=-\frac{\sin\,(\theta'-\theta)}{\sin\,(\theta'+\theta)}.$$

Obviously, the square of the second ratio increases continually from an indeterminate value to unity as θ increases from 0 to $\pi/2$, while the square of the first ratio decreases from the same indeterminate value to 0 as θ increases from 0 to $\pi/2-\theta'$, and from this incidence it also continually increases and becomes unity when $\theta=\pi/2$. Since $a''=0$ when $\theta+\theta'=\pi/2$, it follows that the reflected light is then plane polarized with its oscillation direction parallel to the plane of the reflecting surface. Moreover, by making use of the law of refraction, $\sin\theta'/\sin\theta=\mu$, Brewster's law for the relation between the polarizing angle and the refractive index may be derived.

When θ approaches $\pi/2$ (grazing incidence), the amplitude ratios approach unity, the limiting value for no reflecting surface. At normal incidence, $\theta=0$, the ratios are equal (disregarding sign) because the oscillation directions of both components are parallel to the mirror surface. If the incident light is plane polarized and the azimuth of its oscillation direction (X-axis in plane of incidence) is γ, then $b/a=\tan\psi=\tan\gamma$. After reflection, the azimuth (γ'') of the practically rectilinear reflected oscillation is obtained from the relation

$$\tan\gamma''=-\frac{b''}{a''}=-\tan\psi''=-\tan\gamma\frac{\cos\theta'-\theta)}{\cos\,(\theta+\theta)}.$$

Thus at normal incidence and to an observer who always looks in the direction ($-Z$) of the source both before and after incidence (the source being, respectively, real and apparent), reflection rotates the plane of oscillation in a manner remindful of the "from right to left" perversion of a reflected image and $\gamma+\gamma''=\pm\pi$. As θ increases from 0 to the polarizing angle, the rotation, $\pm(\gamma''-\gamma)$, decreases to one-half the value it had at normal incidence, because a'' is then practically negligible. Moreover, since $\cos\,(\theta+\theta')$ changes sign at the polarizing

angle, the rotation continues to decrease and becomes zero when $\theta=\pi/2$.

The effect of the change in sign of cos $(\theta+\theta')$ is the same as that which would be caused by a sudden change from π to 0 in a phase difference between the reflected X- and Y-components (that is, between the oscillation corresponding to a'' and b'') as θ increases through the polarizing angle. Moreover, if the mirror surface is of such a nature that the light reflected near the polarizing angle is elliptically polarized, intermediate phase differences are actually observable, and any change in phase is not abrupt, since it develops more or less gradually as incidence increases and reaches the value $\pi/2$ at or near the incidence $\theta=$arctangent μ. (The sign of the phase difference is not taken into consideration.) Normally, the angle of incidence corresponding to a phase difference of $\pi/2$ would be considered as the polarizing angle, since it is then that the major axis of the oscillation path is parallel to the mirror surface. Obviously, the Fresnel equations in the simple form presented above must be modified for those cases in which the reflected (and transmitted) light is elliptically polarized. The similar expressions developed for the relation between the components in the case of total reflection (a phenomenon which occurs only when $\mu_i>\mu_r$, and after θ' $(>\theta)$ reaches $\pi/2$) are examples of a relatively simple modification [3, p. 358]. Similar expressions are also developed for reflection from metal surfaces. In the development of the equations for such cases, the angles of refraction are treated as imaginary or complex qualities.

In metallic reflection, the incident plane polarized light not absorbed (some light may be transmitted if the mirror is very thin) is reflected as elliptically polarized light at all angles of incidence except normal and grazing. The particular angle of reflection (and incidence), termed the "principal incidence," $\bar{\theta}$, corresponds to the polarizing angle of transparent reflectors in that it is defined as the angle of incidence for which the phase difference between the components in and normal to the plane of incidence is $\pi/2$. Thus at this incidence the major axis is parallel to the reflecting surface. The angle having a tangent equal to the ratio of the axes (B/A) of the reflected elliptical oscillation which corresponds to this incidence is named the "principal azimuth," $\bar{\Psi}$, provided the azimuth, $\gamma_i=\psi_i$, of the incident plane polarized monochromatic light is $\pi/4$(or $3\pi/4$). When these angles are determined for a metallic mirror, the refractive index, μ, and the extinction coefficient, κ, may be closely approximated in many cases by computing them from the simplified equations [1, p. 363]

$$\kappa=\tan 2\,\bar{\Psi}$$

$$\mu\sqrt{1+\kappa^2}=\sin\bar{\theta}\tan\bar{\theta}.$$

Ordinarily the characteristics of the reflected elliptically polarized light are determined at other angles of incidence than $\bar{\theta}$. The equations [4, p. 261] for determining μ_θ and κ_θ in these cases are reduced to the forms

$$\mu_\theta=\frac{\sin\theta\tan\theta\cos 2\psi}{1-\sin 2\psi\cos 2\delta}$$

$$\kappa_\theta = \frac{\sin\theta \tan\theta \sin 2\psi \sin 2\delta}{1 - \sin 2\psi \cos 2\delta}.$$

and require the measurement of ψ (the arctangent of the ratio (b''/a'') of the reflected components normal to and in the plane of incidence) and 2δ (the phase difference introduced between the components on reflection). Moreover, it is assumed, as above, that the incident light is monochromatic and polarized in a plane having the azimuth $\gamma_i = \pi/4 = \psi_i$. In consideration of relations (a), (b), and (e) of eq 9, these equations may also be written in terms of functions of the ratio of the axes of the reflected ellipse and the azimuth of its major axis.

$$\mu_\theta = \frac{\sin\theta \tan\theta \cos 2\Psi \cos 2\gamma}{1 - \cos 2\Psi \sin 2\gamma}$$

$$\kappa_\theta = \frac{\sin\theta \tan\theta \sin 2\Psi}{1 - \cos 2\Psi \sin 2\gamma}.$$

The coefficients, μ_θ and κ_θ, determined experimentally at different angles of incidence, will vary with that angle. The relation between coefficients, μ_0 and κ_0, for normal incidence to those for any other incidence may be simplified greatly by neglecting all squares of higher powers of $\frac{\sin^2\theta}{\mu_\theta^2 + \kappa_\theta^2}$. For most metals the resulting equations

$$\mu_0 = \mu_\theta\left(1 + \frac{\sin^2\theta}{2(\mu_\theta^2 + \kappa_\theta^2)}\right)$$

$$\kappa_0 = \kappa_\theta\left(1 - \frac{\sin^2\theta}{2(\mu_\theta^2 + \kappa_\theta^2)}\right)$$

are adequate in computing the coefficients at normal incidence.

As in the reflection from transparent media, surface films are disturbing factors, and care must be taken to eliminate them as far as possible if the optical coefficients of metals are determined by this catoptric method. Under the best conditions, the method does not yield results with an accuracy comparing to that of results obtained by dioptric methods, but it can be used in cases where they are practically inapplicable.

9. SEGREGATION OF PLANE POLARIZED LIGHT BEAMS

(a) POLARIZERS FROM LARGE CRYSTALS

While a practically plane polarized beam of light is easily obtained by reflection from mirror surfaces on transparent media, the method is, as already stated, inefficient and unsuited for most polarimetric measurements. The resolution of natural light into two equally intense plane polarized beams by double refraction serves, on the contrary, as an ideal method of producing polarized light whenever it is possible to segregate one of the component beams without undue loss of intensity. In some cases this segregation is accomplished to a degree by the crystal itself. Tourmaline, for example, not only resolves natural light into plane polarized beams but also absorbs them

differentially. As a result, a plate of no great thickness (possibly 1 or 2 mm, depending on the crystal) transmits very little more than the extraordinary beam. The oscillation direction in the extraordinary beam lies in the plane containing both the normal to the plate surface and the optic axis. This plane, since it is normal to the face of the plate, is termed the principal section of the refracting surface. Obviously two such plates in series with their principal planes at right angles will almost completely absorb both components, since the extraordinary of the first becomes the ordinary beam of the second.

Polarizers of this sort are not efficient because the transmitted component is also reduced materially in its intensity. Moreover, the differential absorption varies with wave length, and when complete polarization is almost attained with a minimum loss of intensity for one color, the intensities of other colors may in comparison be greatly reduced or the polarization for other parts of the spectrum may be far from sufficient. Similar disadvantages are found in certain artificial polarizers.

Crystals such as quartz and calcite are highly transparent for both beams over a very great range of wave lengths. Consequently, the production of an efficient polarizer requires only the segregation of one of the polarized components by some artificial means which does not materially reduce the intensity of the component. The comparative frequency with which sufficiently large crystals of quartz and calcite are found has caused these materials to become very important adjuncts in all polarimetric work. The smaller divergence between the refractive indices of the component beams in quartz has limited the use of this material in the production of simple polarizers for visible light. However, the difference between the calcite indices is sufficient in some directions through the crystal to cause a comparatively large deviation of the ordinary and extraordinary beams. This large divergence makes it easy to segregate either of the plane polarized beams. In fact, such a beam of plane parallel light may be obtained with a cross-sectional diameter equal to one-tenth the crystal thickness simply by the proper use of diaphragms. Obviously, the procurement of beams having the cross section (or aperture) often required would necessitate the use of unduly large crystals. Consequently, Nicol took advantage of the differences between the refractive indices for the two beams to effect the total reflection of the ordinary beam at an interface formed by a cementing material with an intermediate index, and he thus devised a type of prism which greatly increases the aperture obtainable at the expense of a comparatively slight loss of intensity. Of the various modifications of this prism, some have so nearly the form of the original cleavage crystal that the direction of the optic axis, the principal plane (section) of the faces, and consequently, the direction of the oscillation may be determined approximately by simple inspection.

In a calcite cleavage rhombohedron, the X-direction is the optic axis and makes equal angles with the three edges at either of the two fully obtuse corners formed by the cleavage surfaces. These edges include three facial angles of about 101°55′ at these corners, and the optic axis makes an angle of about 63°44′ and 45°23′ with each edge and face, respectively. When light is incident normally on a face, the ordinary ray (direction of the ordinary beam) passes directly through

the rhomb, as in the case of an isotropic plate; but the extraordinary ray, although deflected, is so directed that a plane containing both rays parallels the optic axis. This plane is the principal optic plane (or section) of the transmitting faces. The principal section for the artificial faces of a nicol prism are similarly determined, and the oscillation directions of the extraordinary and ordinary beams lie, respectively, in and perpendicular to it.

(b) POLAROID

Polaroid, which is a polarizing material in sheet form, consists of submicroscopic needle or thread-like pleochroic crystals of herapathite [7][2] (iodoquinine) embedded in a suitable matrix, such as cellulose nitrate or acetate, and all oriented in the same direction. It may be produced in almost any size desired. According to the patent specifications (U. S. Patent 1,951,664), it may be made in the following manner:

Quinine bisulfate (1.5 g) is dissolved in 50 ml of methyl alcohol, brought to a boil, and stirred while adding 0.525 g of iodine as a 20-percent solution in alcohol. Stirring is continued while a jell forms and until the mass has cooled. The herapathite is rapidly precipitated out of the solution as a jelly of interwoven submicroscopic needles. This jelly is then incorporated in a viscous suspending medium, such as a solution of cellulose nitrate or acetate dissolved in amyl or butyl acetate or other suitable solvent, and stirred until uniformly dispersed throughout. By pouring or flowing a viscous medium of this character, the mechanical forces acting upon the crystals are such that the crystals all turn until their long axis is substantially parallel to the direction of flow. The flowing in some cases is accomplished by extrusion through a long thin die (U. S. Patent 1,989,371) or by flowing past an edge (U. S. Patent 2,041,138). In either case, a flat ribbon-like sheet is obtained, having the crystals all oriented in the same direction. The crystals then behave approximately as a single large crystal the full size of the sheet. The active layer is protected by exterior layers of the cellulosic material or by glass plates.

In the central part of the visible spectrum, the polarization is about 99.8 percent complete, but at the ends of the spectrum, both in the extreme violet and in the extreme red, the polarization is not nearly so good [8]. This results in a faint residual purplish tint in the field instead of blackness when two pieces of Polaroid are accurately crossed, when using an intense white-light source.

In certain applications of polarized light, Polaroid is the equal of the nicol prism and in some cases is superior. It has opened up new fields of application to which the nicol prism is not adaptable.

For one class of work, however, at least in the present state of the art, the nicol prism still has no serious rival, namely in those applications where nearly complete extinction is required, as in precision polarimetric measurements. Here complete polarization is required, and any unpolarized light seriously interferes with the precision of the measurement.

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[2] This substance was named in honor of its discoverer, William Herapath, who studied this material from the standpoint of making polarizing apparatus from it. He was able to obtain single-crystal polarizing plates ½ inch or more square, which he believed would soon entirely supersede the nicol prism and the tourmaline plates then in use (1852) as polarizing media.

For most applications where a bright field or an interference pattern is used, Polaroid is optically as good as a nicol prism and has the advantages of being very thin and not being limited to a comparatively small free aperture, as is the nicol. Instead of displacing the nicol prism, Polaroid finds its most useful and satisfactory applications in those very cases for which the ordinary polarizing prism is least satisfactory or is inadequate. The two polarizing mediums are thus supplementary to each other.

Polaroid is finding use in strain detectors and analyzers, in three-dimensional moving pictures, in removing glare for photographic purposes, and in education. Laminated spectacle lenses containing a film of Polaroid are being used in sun glasses for use both on land and on water, the Polaroid removing glare to a large extent. Being comparatively cheap and rather startling in some of the effects that may be produced, it is serving to arouse public interest in the phenomena of polarized light and its many uses in everyday life.

(c) METHODS OF LOCATING THE PLANE OF POLARIZATION

The extraordinary beam is transmitted by practically all modifications of the nicol; but even so, it is in many cases relatively difficult to determine the position of the principal plane, especially if there is some doubt concerning the type of the nicol in question. In such cases, the approximate direction of the oscillation is easily determined by using a plate of glass as a reflecting polarizer and the nicol as the analyzer to extinguish the light thus polarized. That is, the direction of oscillation in any light that would be transmitted by the prism lies in the prism section which coincides with the plane of incidence to the reflector when the nicol is set to extinguish the plane polarized reflected light, and that section is the principal section of the nicol if it transmits the extraordinary beam.

Under the very best of conditions, it is possible to set a simple nicol with a very satisfactory precision in the position for the extinction of plane polarized light. These conditions are, however, seldom realized in the performance of polarimetric measurements. Consequently, in order to increase the precision of the setting, the simple nicol has been so modified (or used in combination with a half nicol) that two half-fields rather than a practically uniform field appear. In many cases, these modifications (described elsewhere in detail) may be used either as polarizer or analyzer, although their use as polarizers is, with certain exceptions, considered preferable, and even necessary, in some polarimetric instruments. As polarizers these special "halfshade nicols" produce, in effect, two parallel and almost equally intense beams of plane polarized light with their oscillation directions mutually inclined at a small angle. In making observations, the simple analyzing nicol, instead of being set for extinction, is so adjusted that its polarizing plane divides this very acute angle between the oscillation planes of the two parts of the polarizer and at the same time makes the corresponding half-fields appear equally intense. If the beams from the polarizer are equally intense, the polarizing plane of the analyzer bisects the angle between their oscillation directions for a matched setting.

Many of the generally used types of halfshade nicols, and especially those composed of a full and half nicol, do not yield the

equality of intensity required to cause this bisection of the half-shade angle at match to an exactitude that is within the precision of a setting on matched fields. That is, the polarization plane of the analyzer set for match always lies closer to the oscillation direction of the beam with the more intense maximum than it does to that of the beam with the less intense. The magnitude of this deviation from actual bisection is precisely determined with difficulty, and there is consequently always some uncertainty concerning the actual positions (azimuths) of the oscillation directions of the two beams from a halfshade polarizer with respect to any chosen reference plane. Fortunately, in simple polarimetry, which is concerned chiefly with rotations of the plane of polarization, this uncertainty has no significance. In other cases, especially if they involve elliptically polarized light, it may be so troublesome that it is necessary to use a type of halfshade nicol that transmits two beams of the same intensity. Even then it is advisable to use the halfshade as the analyzer and the simple nicol as the polarizer, since it is obvious that the analysis of the elliptical polarization produced by any agent of unknown characteristics will be simpler if that agent acts only on a single uniformly plane polarized beam of light with a definitely known azimuth. In general, however, the use of a "halfshade" as an analyzer makes it more difficult to produce the necessary sharpness of division between the half-fields.

In measurements on elliptically polarized light, it is usually not only necessary to know at all times the precise relative angular position of the principal plane of the polarizer with respect to the bisector of the angle between the principal planes of the analyzer, but it is also necessary to determine with great precision its angular position with respect to other directions or planes, such as the direction of lines of electric or magnetic force, the planes of incidence of mirrors, or the principal planes of crystalline plates that are being tested or used as auxiliaries. For this reason it is always desirable, and sometimes necessary, to mount not only the analyzer but also the polarizer in circles that are so constructed and graduated that the nicols may be rotated through 360° and that any rotations may be measured to 0.01° or less. When such circles are a part of a combined polarimeter and spectrometer, some of the methods which have been used for determining the azimuth of the principal plane of the polarizer with respect to some reference direction in the instrument are easily employed.

In the M'Connel method [9] for setting the polarizer at a known azimuth, it is well to remove the polarizer temporarily from the collimator circle, since that nicol and the glass prism or plate (used in alining the axes of telescope and collimator perpendicular to the vertical axis of the polarimetric spectrometer by the Gauss eyepiece method), together with its supporting table, are replaced by an auxiliary nicol prism mounted in a suitable holder that fits the table mounting. This auxiliary nicol with its axis and the common axis of telescope and collimator alined is set so that its principal plane (approximately located as described above) makes a small angle with the vertical axis. The halfshade analyzer (its telescope at this stage being focused on the halfshade field and not as in the alinement tests for parallel light coming from the collimator) is then set for a match on the plane

polarized light being transmitted from the collimator by the auxiliary polarizer. After obtaining this setting, the circle of the prism table is rotated through 180°, so that the auxiliary nicol is reversed end for end, and a new setting of the analyzer is made. It is clear that the difference between the settings taken before and after the reversal is double the small deviation of the principal plane of the polarizer from the vertical axis. Consequently, a setting midway between these settings will yield a match on plane polarized light only when the principal plane of the polarizer contains the vertical axis. The auxiliary nicol is therefore removed and the collimator polarizer is replaced in its circle and rotated until the match for that setting of the analyzer is accomplished. This gives the polarizer setting on its circle for zero azimuth of its principal plane, and with this setting known, any other desired azimuth can be obtained to the degree of precision afforded by the sensitivity of the halfshade system and the analyzer and polarizer circles.

Polarization by reflection at the polarizing angle of incidence from specular surfaces on transparent materials has also been used [10, 11] to determine the position of the polarizer for zero azimuth. When the reflecting surface of the glass alining prism or its equivalent contains the vertical axis and its polarizing angle of incidence is known, the setting of the analyzer corresponding to zero azimuth of polarizer is easily obtained by an analyzer match on light reflected at that incidence. For this test the incident monochromatic light may be either polarized or natural; but if it is plane polarized, the azimuth of the principal plane of the collimator nicol with respect to the plane of incidence must not be too small, since the intensity of the reflected light will then be so low that a match setting of the analyzer is impossible.

When the polarizing angle of the reflector is unknown, it, and also the zero azimuth, may be determined with a precision approximating that of procuring an analyzer match if a series of observations is made for two or more azimuths of the polarizing nicol and at two or more angles of incidence for each azimuth. The azimuths (not exactly known) of the polarizer's oscillation plane with respect to the plane of incidence should be equally distributed above and below zero but not so near that observations are difficult. The angles of incidence should be chosen in about equal numbers on each side of the only approximately known polarizing angle and should not depart from it by more than a few degrees except in preliminary observations. When the observations (angles of incidence and analyzer settings for match) are plotted, the curves (almost straight lines for a narrow range near polarizing incidence) will intersect at the polarizing angle, and the analyzer reading corresponding to this incidence is the analyzer setting for matching on light polarized in the plane of incidence.

Although a graduated collimator circle for the polarizer is advantageous, it is obvious that none of these methods require this, since all necessary azimuth readings may be referred to the analyzer circle. Moreover, once the analyzer setting for light polarized in the plane of incidence is obtained, the polarizing spectrometer may be moved about and used to set the principal plane of polarizers in other instruments with respect to vertical, provided the spectrometer is supplied with adequate leveling devices, which assure a coincidence of its axis with that direction.

10. PRODUCTION OF ELLIPTICALLY POLARIZED LIGHT

(a) BY DOUBLY REFRACTING PLATES

Doubly refracting plates for the production and compensation of elliptically polarized light can be prepared from either uni- or bi-axial crystals. Strained plates of isotropic materials, since they show the so-called "accidental double refraction," are also often used in polarimetric instruments instead of crystalline plates.

Doubly refracting plates from uniaxial crystals are usually cut parallel to the optic axis. Consequently, a beam of plane polarized light normally incident on such a plate is, in general, resolved into two undiverging plane polarized components, the extraordinary with its oscillation plane parallel to the optic axis (X- or Z-axis, depending upon whether the crystal is optically prolate or oblate) and the ordinary with its oscillation plane parallel to the optic normal.

If the plate is from an optically oblate crystal, the extraordinary component traverses it with the greater velocity, $\mu_e < \mu_o$. If by convention the direction of the faster oscillation is chosen as the reference direction in the plate, the optic axis (X-axis), parallel to that direction in this case, should for convenience be marked "fast." In the case of plates from optically prolate crystals, $\mu_e > \mu_o$ and the optic axis (Z-axis) is the direction of the slower oscillation and should be marked "slow."

If the amplitude of the incident rectilinear oscillation is "a", and its azimuth with respect to the fast axis of the plate is γ_p, the amplitudes of the components in, and perpendicular to, that axis are $a \cos \gamma_p$ and $a \sin \gamma_p$ at incidence. Neglecting loss by absorption and reflection, the amplitudes are unchanged on emergence from the plate, but a phase difference proportional to the plate thickness, D, will have been introduced between the oscillations, which were obviously in phase at incidence. According to eq 3, and since $z=D$, this phase difference, $\delta_p = 2\pi D(\mu_o - \mu_e)/\lambda = \delta_D$ (in an optically oblate plate, for example), and in eq 5 to 9, it is the equivalent of 2δ. Moreover, according to identities of the preceding eq 8, the ratio of the amplitudes $a \sin \gamma_p / a \cos \gamma_p = \tan \gamma_p = \tan \psi$. When δ_p and ψ are known, the characteristics of the resultant elliptical oscillation may be determined from eq 9.

To determine δ_p with the needed accuracy usually requires some precise method of calibration, but its approximate value can be computed from D and the refractive indices if the crystal and the manner in which it was sectioned to produce the plate are known. Moreover, since the difference between the indices increases in general with decreasing wave length, it is usually necessary to determine δ_p at several points in that portion of the spectrum in which the plate is to be used.

Such doubly refracting plates are used chiefly as accessories for polarizing microscopes and for such polarimeters as are used in measurements on elliptically polarized light. These accessory plates are usually rated in terms of the phase difference (or relative retardation) which they introduce between components having some designated wave length.

Although the relative retardation, especially when small, is more commonly expressed in circular degrees (or possible radians), the equivalent number (N) of wave lengths may also be used to designate

the "power" of a plate. For example, a plate having a thickness such that it causes a relative retardation of 360° (2π radians) between components having a wave length λ' may be termed "a wave plate for λ'," or if the relative retardation is only 90°, the term "quarter-wave plate" is generally employed. When the relative retardation is even smaller, the terms "10° elliptic compensator" or "4° elliptic halfshade" (as examples) are often used to designate not only the power of the plate but also its purpose.

Serviceable doubly refracting plates may be made from almost any sufficiently large, transparent, anisotropic crystal, provided the difference in the refractive indices for the plane polarized component beams is not so great that a plate producing the required relative retardation is too thin and fragile. For example, a wave plate cut from calcite parallel to the optic axis would be quite thin, and since $N=\delta_p/2\pi=1$ for a wave plate, the thickness can be computed from the relation $D=\lambda'/\mu_o-\mu_e$. For a calcite plate cut in such a manner, the difference in the indices is about 0.172 for sodium light, and consequently D is roughly 0.0034 mm. In the case of quartz (optically prolate) $\mu_e-\mu_o=0.0091$ approximately for sodium light, and for a corresponding wave plate cut parallel to the optic axis, D is roughly 0.065 mm.

Mica, a monoclinic (pseudohexagonal) crystal, is much used in making doubly refracting plates (especially those having very low relative retardations). This follows because its perfect basal cleavage, giving thin elastic sheets, makes it relatively easy to prepare fairly uniform plates of considerable area and of almost any needed thickness. The acute bisectrix (X-axis) of this mineral makes an angle with the normal to the plate (basal cleavage) surface that ranges between 0° and 2°, depending on the specimen, while the angle between the optic axes is about 70°. The Z-axis is consequently the oscillation direction of the "slow" component and the Y-axis that of the "fast", and the corresponding refractive indices may be used for computing the approximate thickness of mica wave plates. While these indices vary considerably with the specimen, their difference for sodium light is of the order 0.004, and D for a wave plate at that wave length is consequently about 0.14 mm. Accordingly, the thickness of a mica quarter-wave plate for sodium light is about 0.03 mm [5, p. 352], and of a 2° halfshade, about 0.0008 mm. Some of the thinnest mica halfshades used show the brilliant first-order interference colors by reflection in white light.

When designed for use as accessories, thin doubly refracting plates, or even thick ones not made of comparatively hard crystals, should be mounted in Canada balsam between glass cover plates, unless the nature of the measurements requires other mounting materials. The cover plates should obviously be free from strain, since otherwise the "accidental" double refraction modifies the power of the enclosed plates. This modification can be particularly disturbing, since it is seldom uniform over the plate aperture. Multipel reflection between the surfaces of the plate or of its covers is another factor which sometimes causes certain annoying modifications in the performance of the plate. In many cases the first of the multiple images may become brighter than the primary image as the "matching" of a halfshade field is approached, and a setting for "complete" extinction is impossible if the images coincide.

Tilting a doubly refracting plate with respect to the light beam changes the effective order of the plate. Consequently, when the measurement undertaken depends on previous or independent calibrations of such a plate, it is necessary to maintain the light beam normal to the plate unless the tilting is controlled and made a part of the measuring procedure. Finally, in very precise measurements by certain methods, it may been necessary to consider other factors (temperature effects, for example) which might affect the order of a plate to a degree not compatible with the desired precision.

(b) BY ELECTRIC AND MAGNETIC FIELDS

Besides doubly refracting crystals and strained media, metallic reflection has also been mentioned as producing marked elliptical polarization. Because of their theoretical significance rather than their practical importance in polarimetric measurements, mention should also be made of the elliptical polarization effects observed when media in magnetic and in electric fields are traversed perpendicular to the lines of force by polarized light. The Zeeman effect is another condition which should not be passed without mention, because in this particular case polarized light is apparently emitted by a source. The effect is observed when incandescent vapors emitting line spectra are placed in strong magnetic fields. Lines unpolarized under normal conditions of emission are so affected under the influence of the fields that they are resolved into polarized component lines by a spectroscope. In the simplest of many more or less complicated effects, there are two oppositely rotating circularly polarized component lines when the source is viewed along the lines of magnetic force, and three plane polarized component spectral lines when the viewing is at right angles.

As compared to the normal unpolarized spectral line, the component circularly polarized in the direction of the amperian current producing the magnetic field is decreased in frequency, the other is increased. On the same basis of comparison, the central plane polarized component (oscillation plane parallel to the magnetic force) is unchanged in frequency, while the other two (oscillation planes perpendicular to the force) suffer the same changes in frequency as the circularly polarized components.

11. MEASUREMENTS ON ELLIPTICALLY POLARIZED LIGHT

From eq 5 to 10 it is obvious that in order to determine the oscillation characteristics of a given beam of elliptically polarized light, it is necessary to measure two out of the four following elements of the representative ellipse. These determinative elements are the ratio ($\tan \Psi$) of the minor to the major axis; the azimuth (γ) of the major axis with respect to some chosen reference plane; the ratio ($\tan \psi$) of the amplitudes of the rectangular rectilinear oscillations which are obtained when the elliptical oscillation is resolved into plane polarized components in and parallel to the same reference plane; and the phase difference (2δ) between such components. If the elliptical polarization is produced from a plane or elliptically polarized light beam by some agency such as a doubly refracting plate, it is obviously necessary to determine not only the characteristics of the emergent light but also those of the beam incident on the plate. Moreover, the azi-

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muth (γ_p) of the principal plane of that plate with respect to the reference plane must also be known. In general, therefore, there are five measurements which must be made. In addition, the location of the chosen reference plane may require several measurements, as already shown.

The apparatus for the determination of these various elements consists of a polarizer for producing the oscillation form of the incident beam and an elliptic analyzer capable of yielding such measurements as may be required to analyze the oscillation characteristics of both the incident and emergent beams. When combined, the resulting instrument is adapted for practically any required polarimetric measurements on a polarized beam with any definite oscillation form from plane to circular. Such an instrument is, therefore, essentially a universal polarimeter.

(a) ELLIPTIC POLARIZERS AND HALFSHADES

Very often the polarizer is simply a nicol prism. In such a case $\tan \Psi_i = 0$ if $\gamma_i = 0$. However, the polarizer usually is set in such a position with respect to the principal plane of the doubly refracting plate under investigation that $\pm\gamma_i = \pi/4$ or $3\pi/4$. In that case, this principal plane is the reference plane and $\gamma_p = 0$. Moreover, $\tan \Psi_i = \pm 1$ and $\delta_i = 0$.

In some cases the polarizer consists of a nicol followed by a quarter-wave plate, which is so set that it produces circularly polarized light, which may have either a right or left vector rotation. With this device, γ_i, at incidence on a second plate, is obviously undeterminate, while $\Psi_i = \psi_i = \pi/4$ and $2\delta_i = \pi/2$.

Seldom is there any advantage in using incident beams that are other than plane or circularly polarized, unless an elliptic halfshade following the nicol is introduced. In such cases the incident beam is divided into two parts, with different ellipses representing their polarization. The axis ratios of these ellipses may be practically equal or different. When equal, the vector rotations in the two parts of the beam are opposite. When the ratios are different, that for one part of the beam is generally zero and that for the other is small. Usually, with such halfshades, the azimuths, γ_i, for both parts of the beam are practically that of the light emerging from the polarizing nicol. Balanced halfshades produce the condition in which the axis ratios for the two parts of the beam are equal, and the Bravais [1, p. 348] biplate is an example. The Brace elliptic halfshade [12] is an example of the unbalanced type.

(b) ELLIPTIC ANALYZERS

The elliptic analyzer usually consists of an elliptic compensator and a following nicol prism, while in some cases an elliptic halfshade is introduced between these parts rather than in the polarizer. Moreover, the simple nicol is sometimes replaced by a split (halfshade) nicol. The use of both halfshades divides the field (or beam) into four parts which must be matched in intensity for an analyzer setting. Except during initial adjustments in the assembly of the analyzer, the elliptic halfshade is bound to the nicol and does not rotate independently. However, both the compensator and the nicol must be capable of independent rotation. A universal analyzer containing the three parts has been designed and described by Skinner [13].

(c) ELLIPTIC COMPENSATORS

Various kinds of elliptic compensators have been used but, in general, these may be divided into two classes—variable- and constant-order compensators. (The order of a compensator or halfshade is the relative retardation it produces, expressed in wave lengths.) Well-known examples of the first type are the Babinet and strain compensators. It seems that the first of these was designed by Babinet merely to detect elliptically polarized light and was later adapted by Jamin for use in actual measurement. A more or less detailed description of this compensator can be found in most texts on physical optics, and an excellent example of its use is found in Drude's Investigation of the Optical Constants of Metals [14, 15].

With the original form of Babinet compensator, the use of an elliptic halfshade is not feasible because the field of view presents a series of bright and dark bands, which are indicative of the compensator order in the different parts of the beam and which are shifted when the ellipticity of the light is changed. With the Soleil modification it is, however, possible to use an elliptic halfshade because, in effect, each band is so broad that it covers the whole field, which therefore presents a practically uniform intensity.

The strain compensator also presents a field of uniform intensity and is often used in conjunction with an elliptic halfshade. Such a compensator consists of a plate of glass (or other suitable transparent isotropic material) which is so mounted that it may be subjected to positive and negative compressions in a direction perpendicular to the light beam and in the desired azimuth. Within reasonable limits, the relative retardation of such a compensator is proportional to the compression.

The quarter-wave plate (Senarmont's compensator) and the Brace elliptic compensators, which have much smaller orders, are examples of fixed-order compensators. These are both adapted to use with elliptic halfshades. In fact, high precision of measurement with any uniform-field compensator depends on such use. With such combinations a sensitivity has been claimed which permits, under best conditions, the detection of a change in axis ratio equal to 0.0001.

(d) FUNCTIONS OF ELLIPTIC COMPENSATORS AND HALFSHADES

The usual function of a compensator is to restore elliptical polarization to plane polarization. A quarter-wave plate compensator or its equivalent is obviously capable of so reducing any elliptical polarization, simply by making either the fast or slow axis of the compensator to coincide with the major axis of the light oscillation. The positions of the compensator axes in such complementary settings yield the data required to determine γ for the major axis. Moreover, the azimuths of the oscillation planes of the resultant plane polarized beams, corresponding to the two complementary settings, may be determined by the analyzer nicol and the major axis bisects the acute angle between these planes. This acute angle is, therefore, equal to 2Ψ.

If the order of the compensator is less than a quarter wave, it will reduce elliptical oscillations to plane polarized light only when $2\Psi \gtreqless 2\delta_c$, the order of the compensator expressed as angular retardation. (See eq 9a, where, if δ is replaced by δ_c, it is evident that the maximum Ψ for a given δ_c is reached when $\psi=\pi/4$ or $3\pi/4$ and, therefore, when $\sin 2\delta_c=\sin 2\Psi$).

As with the quarter-wave plate, there are complementary settings of the compensator, each of which results in plane polarized light and yields its own particular nicol setting. The Stokes method [16] uses these four settings (two of the compensator, C_1 and C_2, and two of the nicol, N_1 and N_2) for determining not only γ and Ψ but also $2\delta_c$, if the compensator is uncalibrated.

With the nicol and compensator only, it is impossible to determine when the latter has fully reduced (or compensated) the elliptical polarization. The function of a balanced elliptic halfshade is to indicate by a matched field when this compensation is complete. That of the unbalanced halfshade is similar, except that it indicates when the axis ratio of the oscillation leaving the compensator has reached a small definite value. As in ordinary polarimeters, the function of the nicol halfshade is to increase the precision of settings on the major axis of the plane (or the practically plane) polarized light emerging from the compensator.

Three different designs of the apparatus for determining C_1, C_2, N_1, and N_2 are possible. That is, the nicol and compensator may be borne on circles or verniers that rotate independently, a rotating circle which carries the nicol and also a rotating vernier for bearing the compensator, or the relation of nicol and compensator to circle and vernier may be reversed. This last design was that used by Stokes. Consequently, according to his method, $\frac{(C_1+C_2)}{2}-\pi/4$ gave the reading which would make the axes of the compensator and ellipse coincide. Moreover, if $C_2-C_1=c$ and $N_2-N_1=n$ are written, and if a balanced halfshade is used, then $\cos 2\delta_c=\frac{\tan n}{\tan c}$ and $\cos 2\Psi=\frac{\sin n}{\sin c}$. If an unbalanced halfshade is used, these formulas must be modified. The modified forms have been developed by Tuckerman [17] and by Skinner [13].

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III. MEASUREMENT OF ROTATION IN CIRCULAR DEGREES

1. POLARISCOPES WITH CIRCULAR SCALES

(a) HISTORY OF DEVELOPMENT

About the year 1669 Bartholinus [1] discovered the double refraction in Iceland spar. A few years later the polarization of light was first noticed by Huygens [2] while repeating Bartholinus' experiments, but the phenomenon remained an isolated fact in science for more than a century afterwards. In the period 1766 to 1777 M. l'Abbé Alexis Marie Rochon [3], using doubly refracting prisms, perfected a device for measuring small angles with a precision 0.1 of 1 second. With this apparatus, constructed of rock crystal, he measured small angles, such as that subtended by the diameter of a planet, and with a similar one constructed of Iceland spar, he measured the diameter of the sun. His device consisted of a prism cut from a doubly refracting crystal in a direction to give maximum separation to the two rays. In addition to producing an angular separation of the two rays, the prismatic effect spread each of the rays into its spectrum. This latter being undesirable, Rochon added another equal glass prism in reverse position to achromatize the prism. He thus obtained un-

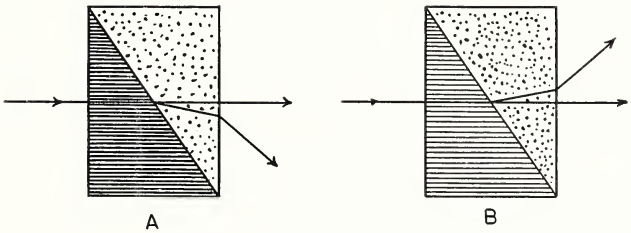


FIGURE 1.—*Rochon's double-image prism, indicating diagrammatically how the extraordinary ray diverges when the prism is constructed of calcite, A, and of quartz or rock crystal, B.*

colored images and still retained the angular deviation between the two differently refracted rays.

He later found that more nearly perfect achromatism was obtained if the second prism was made of the same material as the first but cut in such a direction that the light passed through it along the optic axis, i.e., the direction of no double refraction.

In one form of Rochon's micrometer, this acromatized prism was placed in the tube of his telescope in such a manner that it could be moved back and forth along the axis of the telescope. The telescope was sighted upon the object to be measured and the two images brought just into contact by movement of the prism along the telescope axis. The constants of the prism and its position in the telescope gave the value of the angle being measured.

Rochon appears to make no mention of the fact that the two rays produced by his prism are polarized. It is probable that he knew this to be true but was not particularly interested in that fact. He was an astronomer and navigator and used his device for astronomical and nautical measuring instruments. However, before he

died in 1817, Rochon had the satisfaction of seeing his device used with great success by a young confrère named Arago, for an entirely different purpose, for the study of polarized light.

About 1808 Malus [4] discovered, accidentally, that light when reflected from the surface of glass, acquires properties similar to those possessed by light transmitted through a plate of a doubly refracting crystal, i.e., it is not the same in all directions around the line along which the ray is traveling, but appears to be two-sided, or "polar"; hence the term "polarization."

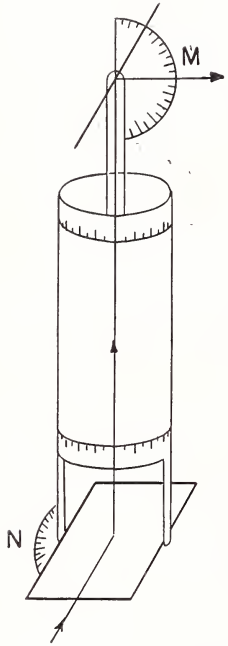


FIGURE 2.—*Diagram of apparatus to illustrate the principle of polarization by reflection discovered by Malus in 1808.*

M and *N* represent mirrors adjustable with respect to the direction of the axis of the apparatus and also rotatable about the axis.

This "two-sideness" of light may be detected by allowing it to fall upon another plane glass plate set at a proper angle. By maintaining the plate at the polarizing angle and rotating it around the beam, the reflected light is seen to vary in intensity as the plate is rotated, and in one position of the plate the reflected light vanishes altogether.

Arago [5], in 1810, discovered the rotation of the plane of polarization of polarized light. He noticed that when quartz, cut perpendicular to the optic axis, was placed between the two inclined plates, the position at which the light vanished was different from that when nothing was between the plates. Arago used Rochon's achromatized doubly refracting prism to good advantage in his studies on polarized light. The glass plate of Malus served as a polarizer, while Rochon's prism served as the analyzer, not only for Arago but later also for Biot. Biot might well be called the father of polarimetry, since it was he who worked out the fundamental physical laws upon which modern polarimetry is based.

Biot [6], in 1812, discovered the proportionality of the rotation to thickness. The apparatus designed by Biot about 1814 for studying polarization in general is shown in figure 3. The polarizer, *M*, was a black mirror set at the polarizing angle and whose mounting, *B*, could be rotated about the axis of the tube, *T*. *B′*, which could also be rotated about the axis of the tube, *T*, carried the mounting, *C*, upon which the sample being studied was placed so that it could be turned in any direction. The light from white clouds of the sky was observed through the analyzer which consisted of an achromatized double-image rhomb of calcite (Rochon prism) mounted upon a divided circle.

This prism, in general, produced two beams, one of which being undeflected was used, while the other, being deviated by an amount depending upon the angle of the doubly refracting prism, was disregarded. This probably was the forerunner of the nicol prism, since it seems only another step to make the separation of the two rays so great that one would be entirely lost from the field of view. In fact,

when the nicol prism was invented in 1828, its inventor described it under the title, "A method of so far increasing the divergence of the 2 rays in calcareous spar that only one image may be seen at a time."

For studying the rotation of the plane of polarization in liquids, Biot replaced the tube, T, by supports to carry a tube closed with glass end-plates in which the liquid was placed. His original apparatus was described in 1811–17 [6, 7, 8]. In 1840 he described [9] certain modifications of his more general instrument, together with explicit precautions in using it for measuring the rotation of optically active liquids.

During the period 1815–40 Biot formulated practically all the fundamental laws of polarimetry in use today. He recognized the

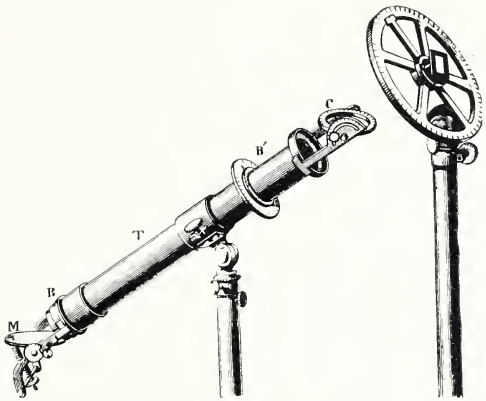


FIGURE 3.—*One form of Biot's original apparatus.*

difference between rotation produced by crystalline structure and that produced by substances when they appeared to have no crystalline structure, i. e., liquids and dissolved substances. The latter he believed to be due to the molecules themselves. He also recognized that each different kind of optically active molecule had a different or characteristic rotatory power. This, within the limits of his experiments, he found to remain the same regardless of whether the substance was in the solid, liquid, or vapor state. In order to have a comparable basis for the purpose of comparing the rotatory power of different kinds of molecules, he calculated from the observed rotation of each substance the rotation for unit length and unit density. This he called "molecular rotation" or "molecular rotatory power" because it had to do with the molecule rather than crystal structure, and he represented it by the symbol $[\alpha]$. By his definition of $[\alpha]$ for the case of pure substances, $[\alpha]=\alpha/\text{density}\times\text{length}$ or using present-day symbols, $\alpha/\rho l$.

In the case of solid substances dissolved in inert liquids, he defined $[\alpha]$ as

$$[\alpha]=\frac{100\times\text{rotation}}{\text{weight }\%\times\text{density}\times\text{length}}\text{ or }\left(\frac{100\alpha}{p\rho l}\right)\text{ or }\frac{100\,\alpha}{cl}. \qquad (12)$$

In these equations, α is the observed rotation in circular degrees, ρ the density, l the length in decimeters, p the grams of dissolved sub-

stance per 100 g of solution, and c is the grams per 100 ml of solution. It is the hypothetical rotation produced in unit length by 1 g of the active material dispersed in a volume of 1 ml, which in present day nomenclature, is termed "specific rotation." Molecular rotation is the hypothetical rotation produced in unit length by 1 gram-molecule of the active material dispersed in (or condensed into) a volume of 1 ml.

This work of Biot appears to have been the foundation of all polarimetry. From this time on, rapid strides were made in the improvement of apparatus, and there resulted the science of Polarimetry as we know it today. A few years later, the polarizing plate of black

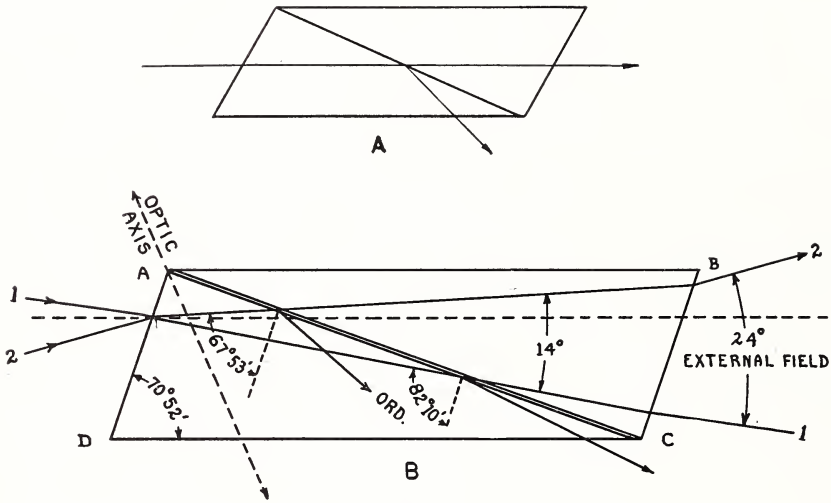


FIGURE 4.—*Original form of the nicol prism.*

A, Diagrammatic sketch; *B*, detailed sketch of limiting rays (1 and 2) and of the various angles. *DAC* and *BCA* are right angles.

glass and the achromatized calcite analyzer rhomb had been replaced by the nicol [10] prism, previously mentioned, which was a far more effective and convenient device for polarizing light than the glass plate. It consisted of a rhomb of Iceland spar cut diagnonally and the two pieces cemented together in such a manner that one of the doubly refracted rays is reflected to one side, and the other passes on through the prism.

(b) TYPES OF POLARIZERS (FIG. 6) AND POLARISCOPES (FIG. 7)

The simple polariscope of Biot was improved by Mitscherlich [11] and by Ventzke [13], one of whom appears to have been the first to use two nicols, and by Robiquet [12] who added the Biquartz of Soleil [14], thus making the setting dependent upon the transition tint (tiente de passage), and many others. Some transition tint instruments are still in use.

In 1856 Pohl [15] attempted to increase the sensitivity of the simple polariscope by the use of a mica halfshade, but was not entirely

successful. However, his idea was later satisfactorily developed by Laurent [16]. In 1845 Soleil [14] had invented the quartz-wedge compensating system and added it to the polariscope, thus laying the basis for the modern saccharimeter.

In 1860 Reverend William Jellet [17] described the first satisfactory halfshade polariscope. The utilization of the halfshade principle was the first important step in the perfection of the modern instrument. Prior to this, with the exception of the Soleil biquartz transition tint plate, both the polarizing and analyzing devices were simple nicol prisms, the "end point" being determined by setting the instrument for a minimum of light intensity in the field. Jellet's contribution introduced into polariscope design the photometric field. To construct his halfshade device, which he used as the analyzer, he selected a rhomb of Iceland spar several times longer than its other dimensions, and squared off the end faces. He then sliced the resulting prism parallel to its long dimension, BS' and at a small angle, SCD, to the short diagonal $D'D$ of the end faces (as indicated in fig. 6A), reversed the two pieces end for end, and cemented them together (fig. 6B). In this manner he obtained a compound prism (shown in cross section in fig. 6C) whose principal crystallographic section $A'C$ in one half made a small angle to that (CA) in the other half, the principal crystallographic section of each half being equally inclined to the short diagonal of the end face. Diaphragms were placed centrally at each end of the prism. One ray (the ordinary ray O' and O) came straight through, while the other (the extraordinary E' and E) was deviated slightly in each half and diaphragmed out. Thus the light in one half of the field was polarized in a plane making a small angle (about 2°) with the plane of polarization of the light in the other half of the field.

In 1870 Cornu [18] improved upon Jellet's idea by removing a wedge-shaped section from a nicol prism and recementing the two halves. Thus the plane of polarization in each half of the field made a small angle with that in the other half, as in Jellet's prism.

Schmidt and Haensch [19] simplified Cornu's prism by removing the wedge-shaped section from one half only of the nicol prism, the three pieces then being cemented together as before. In mounting, the divided half was placed toward the analyzer, and each part of this half gave light vibrating in a plane, which made an angle equal to the angle of the removed section, with the plane of vibration of the light coming from the other part. This angle is known as the halfshade angle. The field of the instrument thus appears divided into two parts, and the setting is made by turning the analyzing nicol until the parts become of equal intensity. The sensitivity of the instrument depends on the magnitude of the angle of the halfshade. As the angle diminishes, the precision with which a setting can be made increases. However, the total illumination of the field diminishes with the halfshade angle. An angle of about 2.5° is the minimum working value for ordinary conditions of measurement.

The advantage of the halfshade principle was universally recognized, and a number of halfshade polarizing systems were introduced by various investigators. Three of these, the Laurent, the Lippich, and the Jellet-Cornu as modified by Schmidt & Haensch, have been extensively used by polariscope builders.

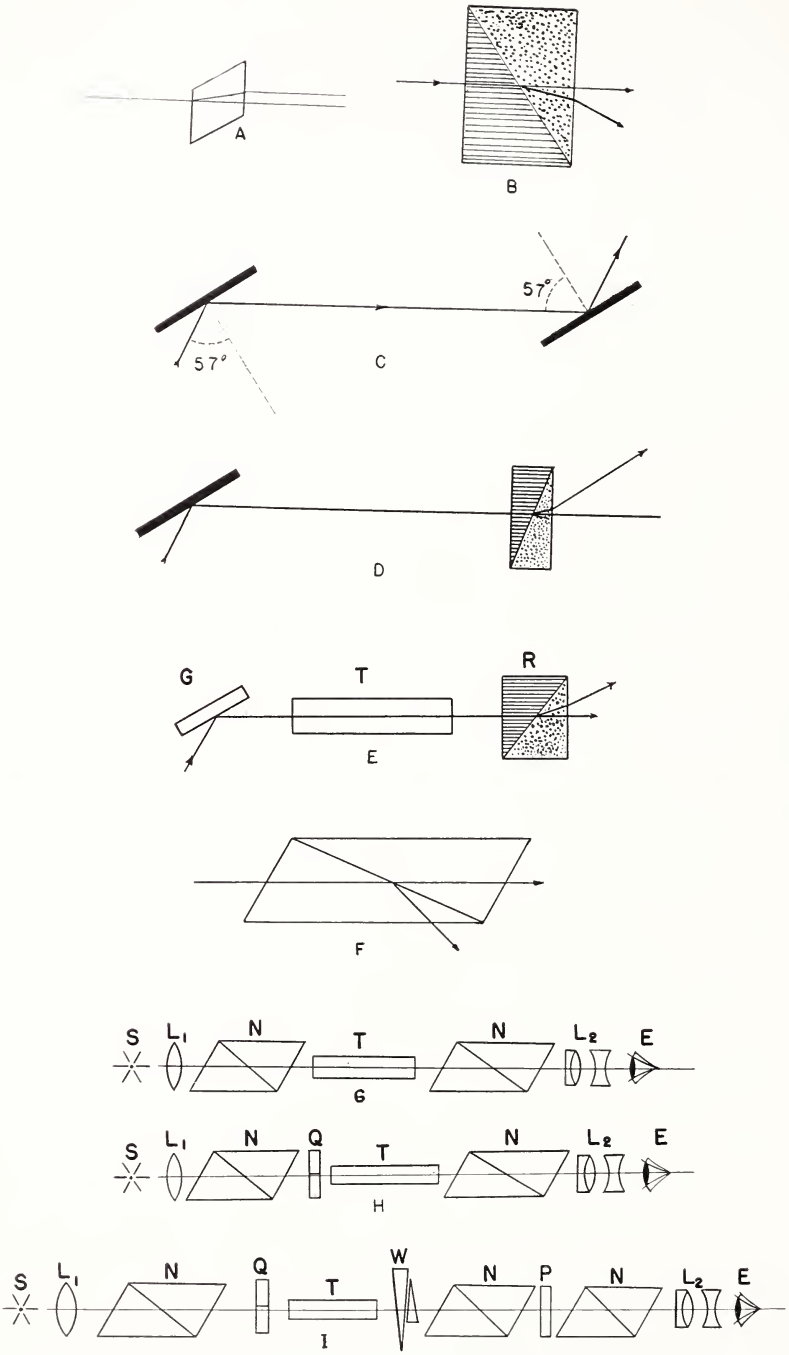


FIGURE 5.—*Graphic representation of steps in the early development of saccharimetry.*

A, (1669) The simple calcite rhomb (Bartholinus).

B, (1783) Rochon's double-image prism.

C, (1808) Malus, polarization by reflection.

D, (1810–11) Arago's discovery of the rotation of the plane of polarization. As a polarizer, he used a plate of glass, and as an analyzer, a calcite prism, achromatized with a piece of glass, operating upon the principle of Rochon's double-image prism with which Arago was familiar.

E, (1815–17) Biot's discovery of the proportionality of the rotation to thickness and concentration, and the formulation of the physical laws upon which modern polarimetry is based. He used apparatus similar to Arago's, placing his solutions in a metal tube closed with glass end plates or cover glasses. *G* represents the glass plate; *T*, the tube; and *R*, the simplified Rochon prism.

F, (1827) Nicol's prism, by which one of the polarized rays (as in the Rochon prism) is eliminated from the field.

G, (1842) Mitscherlich, also Ventzke, improved upon Biot's apparatus by using nicol prisms as polarizer and analyzer, and using various arrangements of lenses, and applied it in the sugar industry.

H, (1845) Soleil's biquartz or sensitive tint plate was added, giving a divided field in which the setting of the instrument was made by matching the colors of the two halves of the field at the "sensitive tint" point.

I, (1845) Soleil's double quartz-wedge compensator was added, enabling white light to be used and laying the foundation for the modern saccharimeter. In *G*, *H*, and *I*, *S* represents the light source; *N*, nicol prisms; *T*, the tube containing the sugar solution; L_1 and L_2, lenses; *E*, the observer's eye; *P*, a quartz plate; *Q*, Soleil's biquartz; and *W*, Soleil's quartz-wedge compensator.

When plane polarized light of more than one wave length traverses an optically active substance, it emerges with the vibration planes of the individual waves all inclined to each other in a sort of fan-shaped arrangement, the violet waves having been rotated through the greater angle. An analyzing nicol, on being rotated, will cut out

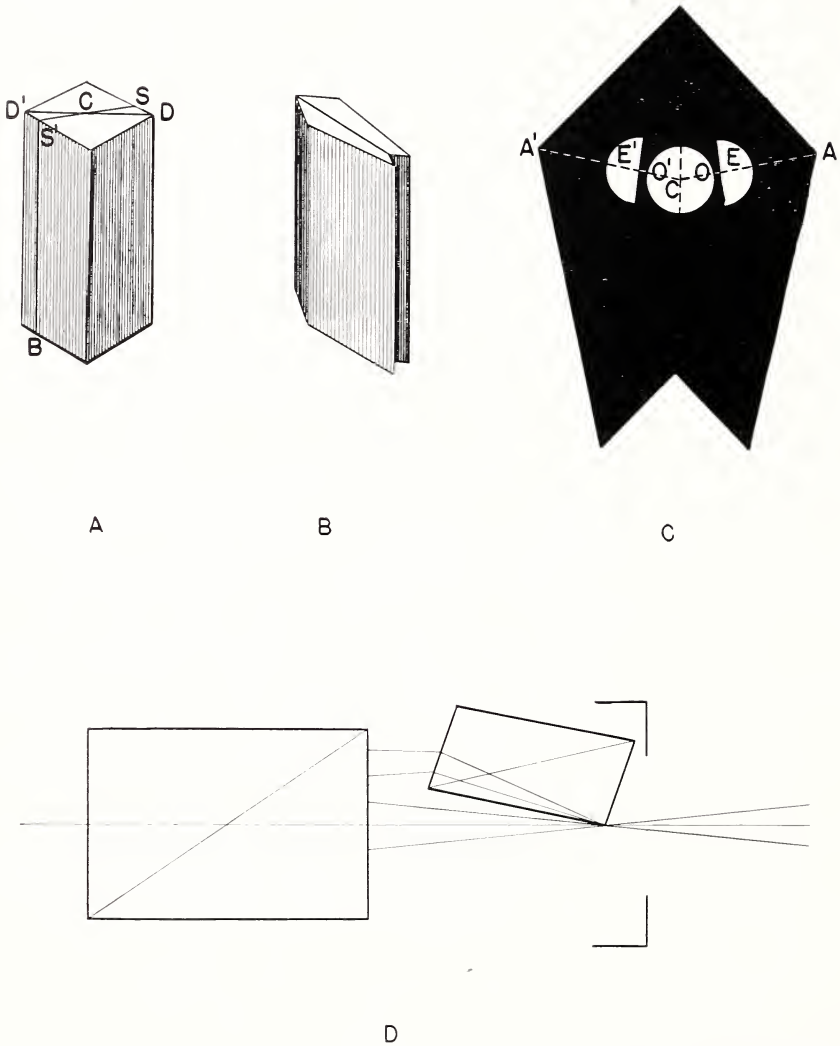


FIGURE 6.—*A, B, and C, Jellet's halfshade device which made the setting dependent upon matching intensities of the light in the halves of the polariscope field; D, Lippich-type halfshade device.*

each wave in turn, but it is impossible to darken the field owing to the fact that some portion of the light from each of the remaining waves passes through the analyzer. If the polarizer be of the divided-field type, it will be found impossible to darken either half of the field, and color will always be present. Thus, in all polariscopes in which

the setting is made by rotating the analyzing nicol, it is necessary that the light source be monochromatic, or at least nearly so.

(1) Laurent and Jellet Polarizers [16,17].—Of the three half-shade polarizing systems mentioned above, the Laurent alone is limited to the use of one single monochromatic source. In this system a half-wave plate, usually a thin plate of quartz cut parallel to the optic axis, covers one-half of the field of the polarizing nicol. In order that the two rays traversing the doubly refracting quartz can combine to give plane polarized light on emergence, they must have an optical difference of path equal to one-half wave length. Thus, the thickness of the quartz must always be such as to bring this condition about, and this form of halfshade can be used only with a light source giving the particular wave length for which this condition is fulfilled. The angular position of the new plane of polarization is slightly different from that of the polarizing nicol, and the conditions for a halfshade are thus established. The advantage of this system is due to its adjustable sensitivity; the halfshade angle, being twice the angle between the optic axis of the plate and the plane perpendicular to the principal section of the polarizer, can be readily varied by rotating the polarizer. Inasmuch as the Laurent polarizer requires a monochromatic source, it is seldom combined with a quartz compensating system. The Jellet polarizer, described above, has a fixed halfshade angle, and therefore the sensitivity cannot be varied. Its advantage lies in the fact that it does not easily get out of adjustment, and does not, in itself, require the use of monochromatic light.

(2) Lippich System [20].—In the Lippich polarizing system, the halfshade angle is formed by two beams of plane polarized light which come from two separate nicols, one of which covers but one-half of the aperture of the other (fig. 6D). If these two nicols are turned until the vibration planes of the light which they transmit coincide, they act as a single nicol (with some reservations). If one of them be rotated through any angle, a halfshade angle is formed equal to that angle. Because of the ease with which the halfshade angle can be varied, as well as the high degree of perfection attained by the opticians in constructing the prisms, we have in the Lippich an adaptable and sensitive polarizing system. The accuracy with which a setting can be made is increased to the extent that the dark dividing line between the halves of the field can be made to vanish. With a broad source of light this condition is very nearly attained in the Lippich. It does not in itself require the use of a monochromatic source.

(3) Sensitive-Strip System.—In 1903 Brace [21] described the sensitive-strip spectropolariscope. In the ordinary nicol prisms the extraordinary ray is utilized. It occurred to Brace that it was possible to reverse this condition and use the ordinary ray. Thus, instead of a film of liquid between two large pieces of Iceland spar, he proposed using a thin piece of spar immersed in liquid and placed in a cell with glass ends, the plate of Iceland spar covering the entire field and being inclined at an angle of 70° to the axis of the system. To obtain a polarizing system similar to the Lippich, it would be necessary to place a second cell with a narrow strip of spar covering one-half of the field, in the position ordinarily occupied by the small nicol of a Lippich system. If such a system could be perfected, it would have many advantages over the Lippich. Among these may be mentioned

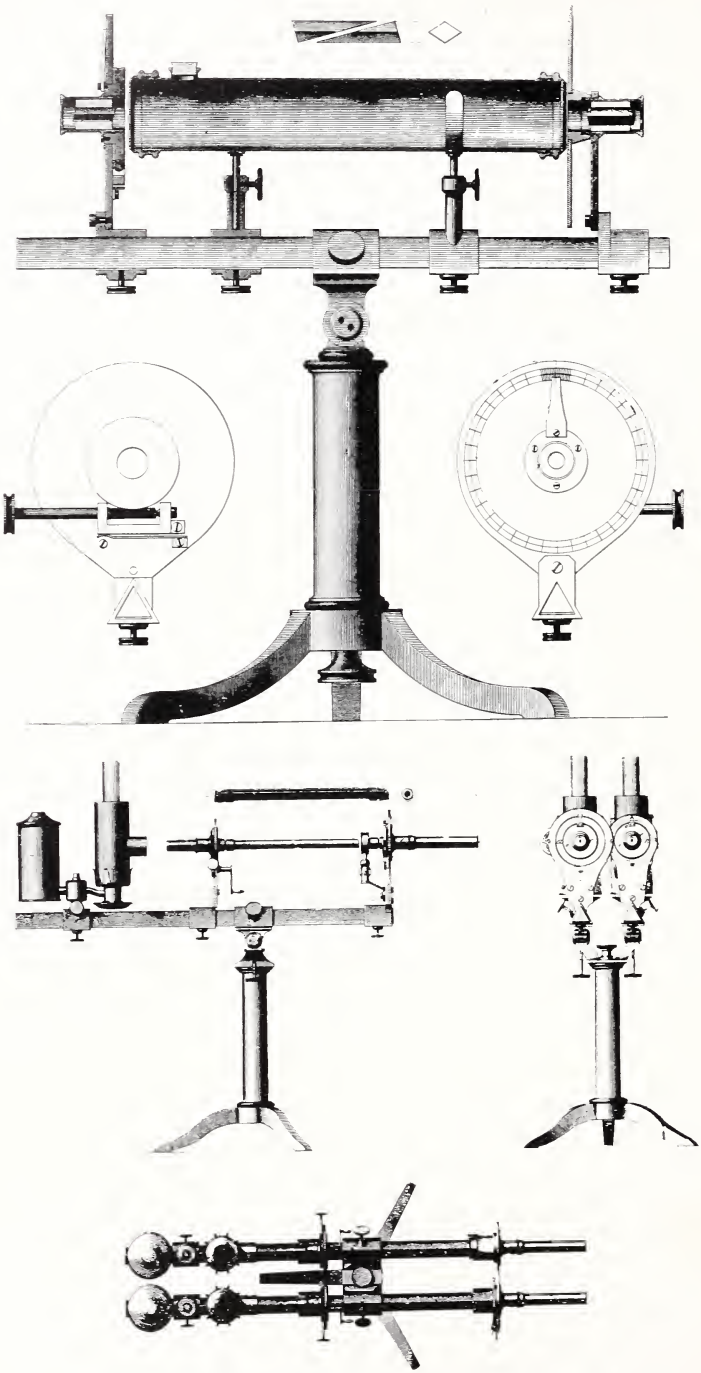
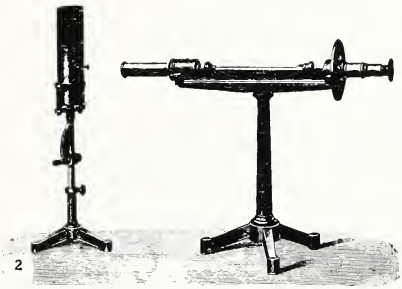
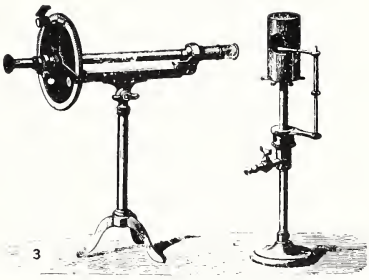
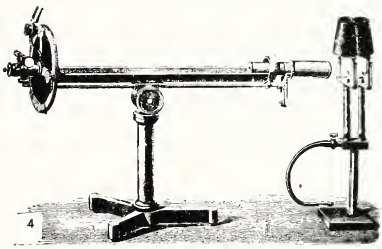
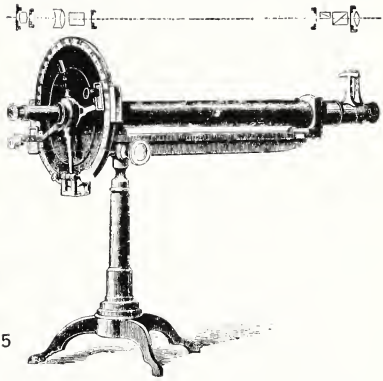


FIGURE 7.—*Early polariscopes.*
Boit's apparatus as modified by Ventzke.









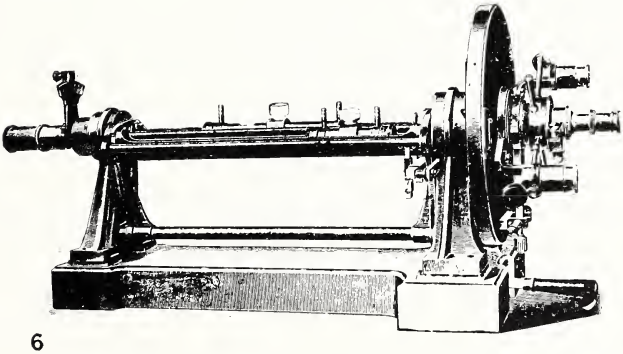
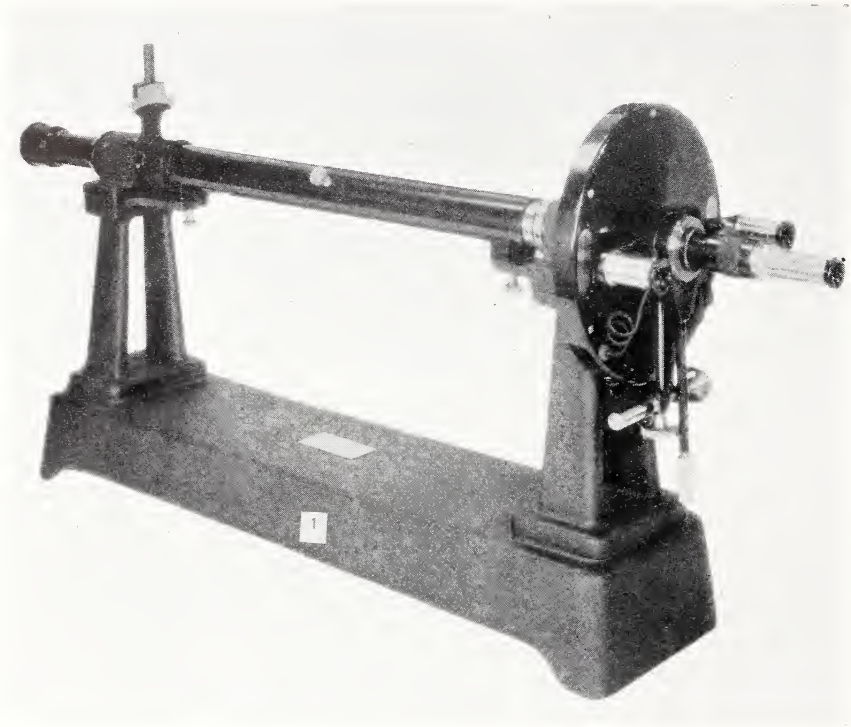


FIGURE 7 (Continued.)—*Early polariscopes.*
2. Mitscherlich; 3, Duboscq; 4, Laurent; 5, Lippich; and 6, Landolt.



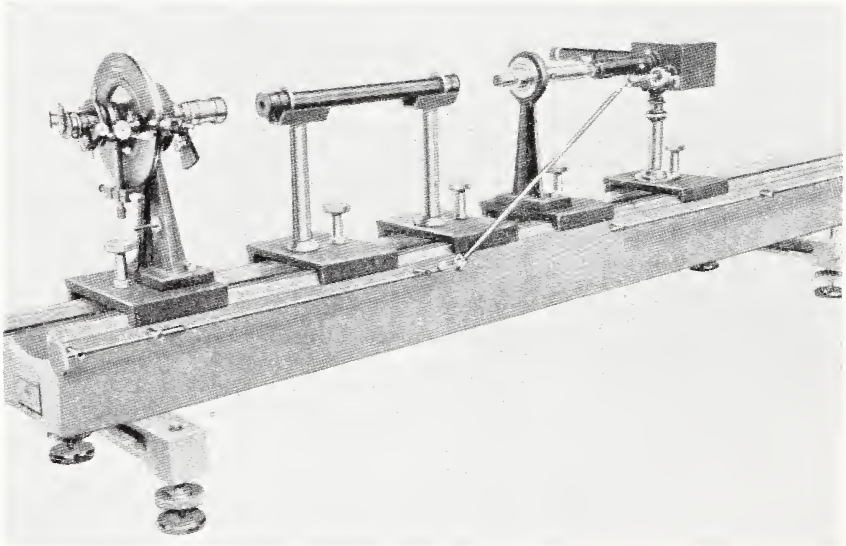
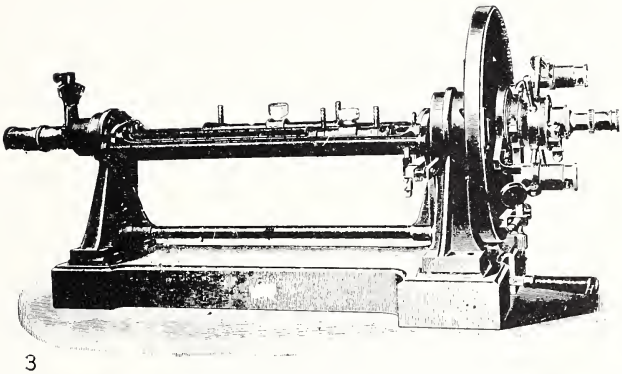


FIGURE 7 (Continued).—*Modern polariscopes.*
Upper, Gaertner; lower, Hilger.



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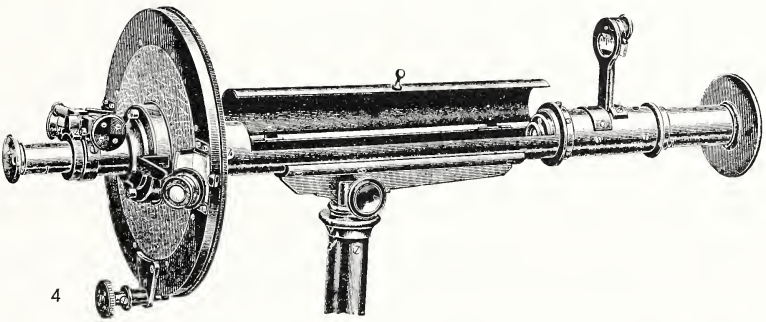

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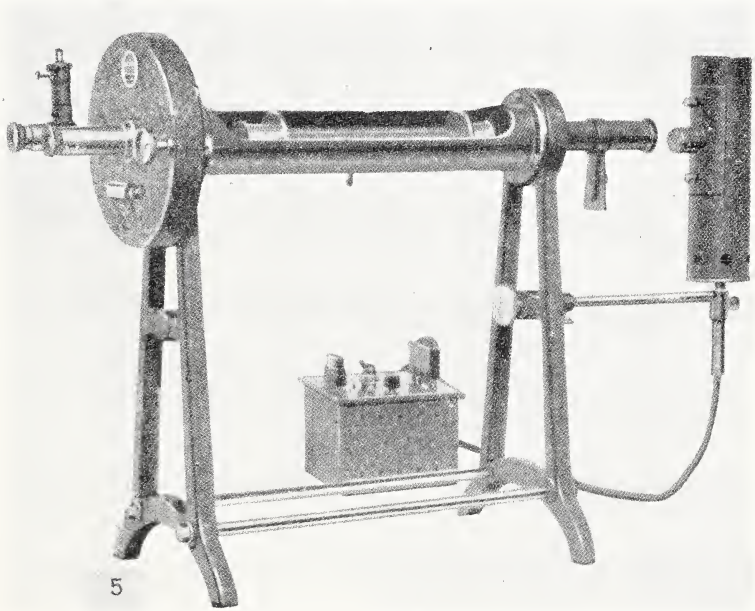


5

FIGURE 7 (Continued).—*Modern polariscopes.*
3, Schmidt & Haensch; 4, Fric; 5, Laurent type (Jobin & Yvon).

the saving of Iceland spar and rectilinear passage of the light through the system. In addition, great sensitivity would be secured because a practically vanishing line would be obtained between the halves of the field, as the small strip of spar need not be over 0.1 mm thick. The device was perfected and used by Bates, who subsequently succeeded in combining the two cells into one. The Brace sensitive-strip spectropolarizing system is the most sensitive yet devised. However, it is rather fragile, and its use is not recommended except in work requiring the highest obtainable precision.

(c) TESTS OF POLARISCOPES WITH CIRCULAR SCALES

Polariscopes with circular scales will be accepted for test (see test-fee schedule 421, p. 553). A thorough examination is given all optical parts. The scale will be checked for as many points as desired.

(d) NATIONAL BUREAU OF STANDARDS EQUIPMENT

Polariscopes with circular scales for measuring absolute rotations are now made by most polariscope builders. The National Bureau of Standards is fortunate in having a large Schmidt and Haensch precision instrument with a silver scale reading to 0.001°. The Lippich polarizing system is unusually good, the larger nicol having an available opening of 15 mm. The instrument is mounted on a cast-iron base 1 m in length. Owing to the necessity for accurately controlling the temperature while measuring rotations, a large air thermostat, consisting of a wooden box 40 by 55 by 60 cm covered with asbestos, is mounted between the polarizing and analyzing systems. Access is had to the interior by means of a small door in the side. The room in which the instrument is located is thermostated at a temperature approximately 1 degree lower than is desired in the polariscope air bath. An electric heater then brings the bath temperature up to the proper point and maintains it there. The heater is made of fine resistance wire wound around a large framework which fits inside the box. See figs. 26 and 27, p. 100–101. The current is controlled by means of an electronic relay operated by a mercury contact, which in turn is operated by toluene contained in a series of glass tubes so constructed and placed as to give a maximum change of volume in a minimum of time when a small temperature change takes place. The air is kept constantly stirred by a small fan. The temperature remains constant to 0.01° C. No mechanical relay of any kind is used, and consequently there is no trouble from relays sticking.

A large Weiss electromagnet, figure 8, equipped with a suitable polariscope is available for the study of magnetic rotation. This magnet is cooled by water circulation, thereby permitted continuous use even when heavy currents are employed.

2. LIGHT SOURCES FOR CIRCULAR-SCALE POLARISCOPES

(a) GENERAL

In accordance with the rapidly increasing use of polarimetry in commercial and scientific work, there has arisen a demand for greater accuracy. The largest source of error in precision measurements is in the light sources. The production and utilization of suitable light sources is by far the most difficult problem with which the polari-

scopist must cope, and it therefore receives continuous study at this Bureau. For many years any sodium source was considered suitable for this work. Then came the so-called light filters of Lippich [22] and Landolt [23]. These filters, however, are open to two severe criticisms: (1) The efficiency of the purification is a function of the intensity of the source, and (2) the available light is reduced by absorption in the liquids used in the cells.

Subsequently, spectrum filtration came into use for precision work. In this method, light from an intense source is passed through an optical system containing a dispersing medium, and only the desired wave lengths are permitted to enter the polariscope.

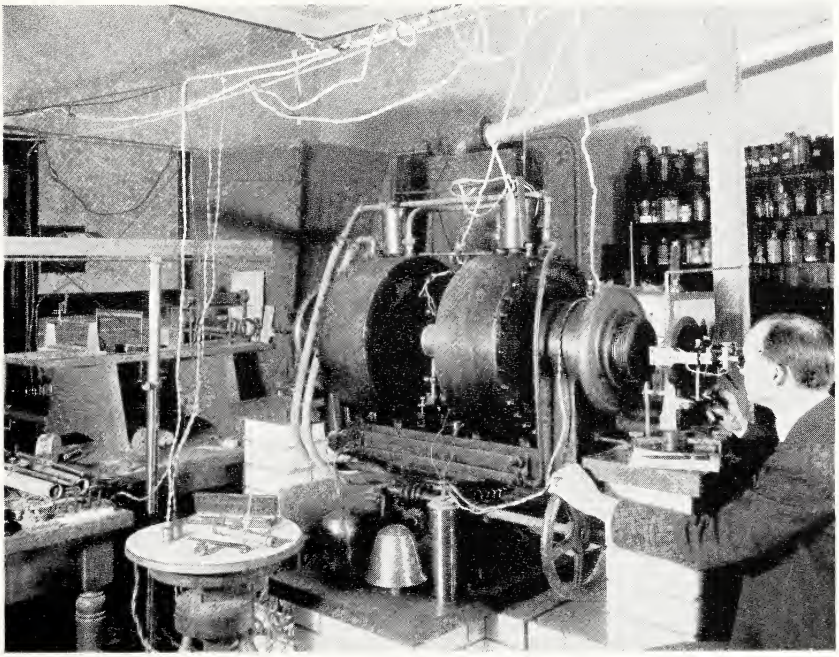


FIGURE 8.—*Large electromagnet for studying magneto-optical effects.*

(b) SODIUM

(1) FLAME.—Until recently the sodium lines have been the one intense source with which a large percentage of the precision work has been done. This source has been used for determining practically all of the polarimetric constants, including the standardization of quartz control plates. Unfortunately, the two sodium lines are difficult to separate from the remainder of the spectrum, and as the flame is intense there is danger of one or the other of the lines reversing. In 1906 [24] a careful study of spectrum lines as light sources for polarimetric work was made at this Bureau. It was found that the lack of intensity, the high dispersion necessary for purification, the presence of other lines of considerable intensity in the neighborhood of D_1 and D_2, as well as the unstable line structure under certain conditions, render this source far from satisfactory. Owing to the great precision

required in present-day polariscopic measurements, intensity is of paramount importance. Even in commercial instruments the half-shade angle is generally not over 10 degrees, which means that the polarization plane of the analyzing nicol is practically at right angles to the planes of the polarizing system and less than 1 percent of the light is transmitted. Thus only a very small fraction of the incident light ever reaches the eye of the observer. After an extensive investigation, the Bureau has found that for an intense sodium flame source the best results are obtained by feeding some form of fused Na_2CO_3 into an oxyhydrogen flame. In utilizing this source a rod of this substance is placed in the flame at one of the positions shown in figure 9. The line structure of the sodium lines obtained by this method was studied with an echelon spectroscope. The lines were found to be extremely sharp and to differ from the arc spectra by the absence of the characteristic haziness in the edges of the lines. If displacements as large as 5 A had occurred, they would have been readily detected. The broadening was at all times symmetrical. In this respect the observations agree with the more recent work of other observers, but are contradictory to the results obtained by Ebert [25], which have been accepted in polariscopic work. By careful manipulation of the flame in position 3, reversals of the lines took place, D_2 preceded D_1 in this respect.

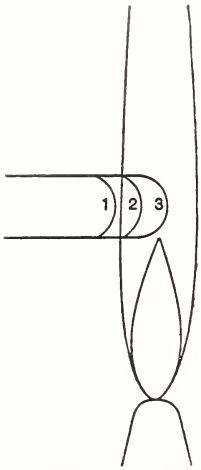


FIGURE 9.—*Oxyhydrogen sodium flame studied at the National Bureau of Standards.*

TABLE 1.—*Structure of sodium lines at different intensities*

Spectrum line	Relative intensity	Width in angstrom units				
		Position 1	Position 2	Position 3		
				Na_2CO_3 melting slowly	Na_2CO_3 melting very rapidly	
D_1	1.0	0.08	0.2	3 to 4	4	[1] 6
D_2	1.6	.08	.2	[1] 3 to 4	[1] 6	[1] 6

[1] Reversed.

It is thus evident that so far as their line structure is concerned, the sodium lines can be depended upon to give a sufficiently definite optical center of gravity up to the point of reversal in position 3 (fig. 9). However, very noticeable variations in polariscopic measurements are likely to be observed with sodium sources at different intensities. These variations, it is believed, are not due to changes in the line structure of the source, but to the difficulty of excluding all impurities in the light, even with a very narrow slit and a dispersion sufficient to separate D_1 and D_2. This extraneous light constitutes a different percentage of the total illumination whenever the intensity of the source varies. It may, therefore, appreciably change the optical center of gravity, thereby giving a different apparent rotation when

the field appears dim than when it appears bright. Aside from the color and stability of the sodium lines up to reversal, there is little in their favor as a polariscopic source. The flame requires the constant attention of an assistant, and even in reversal the intensity is not nearly sufficient to permit the use of the greatest sensitivity of a good polarizing system. The sodium flame sources have been summarized by Landolt [26] in table 2.

TABLE 2.—*Optical center of gravity of sodium light sources, Landolt [26]*

Source of light	Purification	Effective wave length
		A
Bunsen flame with NaBr	10-cm layer of 9 percent $K_2Cr_2O_7$ in water	5920.4
Bunsen flame with NaCl	10-cm layer of 9 percent $K_2Cr_2O_7$ in water	5894.8
Burner with NaCl or NaBr	Lippich filter, $K_2Cr_2O_7$ and $U(SO_4)_2$	5893.2
Sodium	Prism purifications lines D_1 and D_2 only	5892.5
Landolt lamp with NaCl	1.5-cm layer of 6 percent $K_2Cr_2O_7$ in water	5889.4
Bunsen flame with NaCl	10-cm layer of 9 percent $K_2Cr_2O_7$ in water and 1-em layer of 13.6 percent $CuCl_2$ in water.	5889.1
Landolt lamp with NaCl	Unpurified	5880.6

Various types of sodium lamps have been designed to give the greatest possible intensity consistent with a minimum of attention. In the Pribram [27] lamp, fused salt in platinum boats is exposed to a Bunsen flame. When the supply in one boat is exhausted, the boat is withdrawn and a second containing a fresh supply is quickly introduced. Fairly constant illumination is obtained for a long time. In the Schmidt & Haensch lamp, fine platinum wires are bent and inserted into a spoon, the melted salt being drawn up to the point by capillarity to the hottest portion of the flame. In the Landolt [28] type, a Muencke burner (Bunsen lamp with conical wire-gauze top and sufficiently strong air supply to cause the inner dark cone of the flame to disappear) is used. Exposed to the flame are two heavy nickel wires, around the middle of which nickel gauze is wrapped. The gauze is charged by immersing in melted salt. An intense flame is obtained. The Zeiss lamp is a simple and convenient type. Pumice stone saturated with salt is exposed to a Bunsen flame. The position of the pumice stone with respect to the flame is important and is easily controlled by means of a thumbscrew. For a very intense sodium flame the method of molded sticks of fused sodium carbonate previously described, is the best.

(2) ELECTRIC SODIUM LAMP.—Two forms of electric sodium lamps with somewhat different characteristics have recently become available. They are the General Electric sodium vapor lamp [29] made in this country (fig. 10A), and the Osram sodium vapor lamp [30] made in Europe (fig. 10B).

The General Electric lamp must be run from a special transformer housed in the base. The bulb has considerable area which is uniformly illuminated. It must be used on alternating current and is rated at 60 watts.

The Osram lamp, on the other hand, has a comparatively small working area but has a higher intrinsic brightness. It is constructed to operate either from alternating or from direct current (not both, however, as the electrodes are somewhat different in the two types). It uses about 1.4 amperes and may be plugged directly into the power

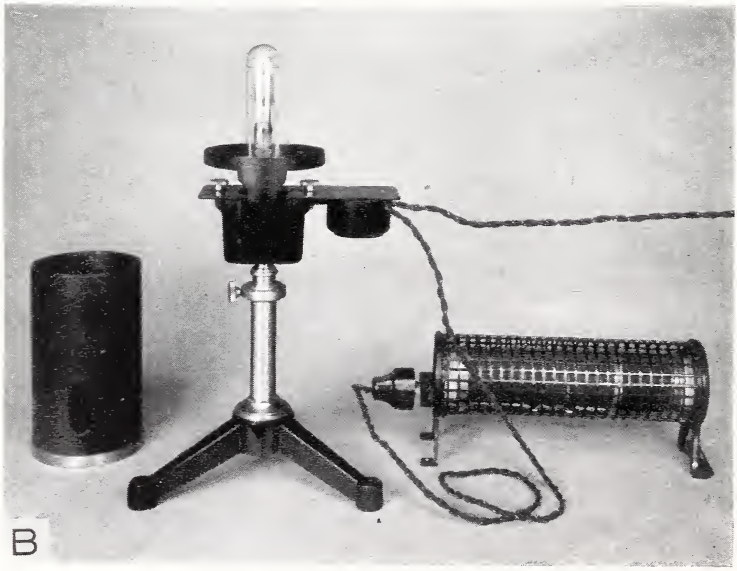


FIGURE 10.—*Electric sodium lamps.*

A, G. E. sodium lamp; *B*, Osram sodium lamp.

line in series with a suitable rheostat only. Its shape makes it particularly adaptable for use in front of a collimator slit. The General Electric lamp is the more suitable where a broader source is required.

Neither lamp gives light consisting of the two sodium D lines alone. While in the light there is very little of the continuous spectrum background which is always present in flame spectra, yet these sources cannot be used without proper purification, as there are four other doublets in the sodium arc spectrum which are ordinarily not observed in the flame spectrum, as shown in table 3:

TABLE 3.—*Wave lengths (in angstroms) of lines in the arc spectrum of sodium*

[The figures in parentheses refer to the relative intensities of the lines as given in "Lines in the Arc Spectrum of the Elements" [31]]

6161 (8) 6155 (8)	D_1=5896 (10) D_2=5890 (10)	5688 (8) 5682 (8)	5154 (6) 5149 (6)	4983 (6) 4979 (6)

In many cases light filters may be used successfully, but where precision rotation measurements are required, spectral purification is needed.

The rigorous requirement as to purity may to some extent be realized when it is known that a quartz plate, which reads approximately 40.000° for D_1 (5896), will read about 40.100° for D_2 (5890). If one is attempting to read to 0.001°, or even to 0.01°, it is obvious that the purity of the light is of much greater importance than has generally been realized.

(c) MERCURY LINES

For the production of the so-called yellow-green line of mercury (λ=546.1 mμ) several types of lamps are available. In all of them, advantage is taken of the fact that mercury vapor, heated to incandescence by an electric current in a vacuum, gives an intense line spectrum. The most important lines, in Angstrom units, and their relative intensities are given [31] as 6908 (10), 5790 (10), 5769 (10), 5461 (10), 4916 (6), 4359 (10), 4078 (8), 4047 (8). Some type of optical dispersion system must be resorted to in order to separate the desired line. At this Bureau the fused-silica mercury lamps originated by Heraeus are used. They may be obtained in almost any desired shape. The straight Uviarc types are particularly convenient. Owing to the relatively high melting point of fused quartz, they can be safely operated at high intensities without water-cooling. *Great care must be exercised not to permit the radiation from these lamps to enter the eyes without first passing through protective glasses.*

The yellow-green line of incandescent mercury vapor, λ=5461, was proposed by Bates [24, p. 243] as the standard source for all accurate polariscopic work. Quartz mercury-vapor lamps as now made are reliable in action. If sufficient care is exercised in preparing the mercury and exhausting the lamps, the characteristic mercury lines only will be obtained in the visible spectrum and with great intensity.

Different observers have found markedly different line structures for the line λ=5461 A, depending upon the method of analysis employed. The map in figure 11 was obtained with the echelon with 1.8 amperes passing through the lamp. The fractional values given are

the relative intensities as nearly as they could be estimated. It was found impossible to decide whether the satellite, −0.24, belongs to the positive or negative side of the primary. When the current was increased to more than 2.1 amperes, the satellite, −0.55, increased in intensity until it about equaled the primary. The difference in wave lengths of the extreme satellites is less than 0.4 A. With a different source, Fabry and Perot [32] found 0.35 A and Houstoun [33] 0.215 A. The distance between D_1 and D_2 of sodium is 15 times 0.4 A. As far as it has been possible to determine, the line structure for the quartz lamp, under widely varying conditions, is such that for polariscopic purposes, $\lambda=5461$ A is a monochromatic source of great intensity and perfect reliability. In measuring a rotation of 250°, no differences could be detected due to changes in the emission, and probably none for much larger rotations. The quartz lamp requires little attention and can be operated indefinitely. Since only the lines $\lambda=5790$, 5769, 5461, 4358, 4078, and 4047 A are important, the difference in wave length is such as to permit of perfect separation of the line 5461 A by even a relatively small dispersion, and without bringing other lines in

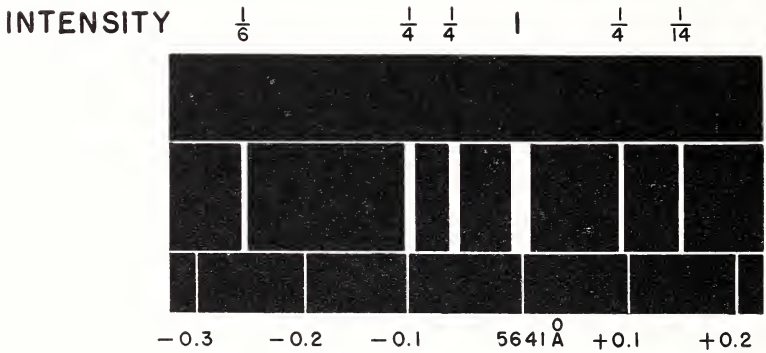


FIGURE 11.—*Map of the yellow-green mercury line,* $\lambda=5461$.

close proximity to the edges of the slit. Hence this source permits the elimination of practically all diffused light.

Since the adoption of $\lambda=5461$ A as the official source for polarimetric measurements by the National Bureau of Standards, its universal acceptance has been recommended by a number of investigators. This Bureau urges its general use, especially when measuring circular degrees in research and precision work, to the end that reliable comparisons may be made between the results of different investigators.

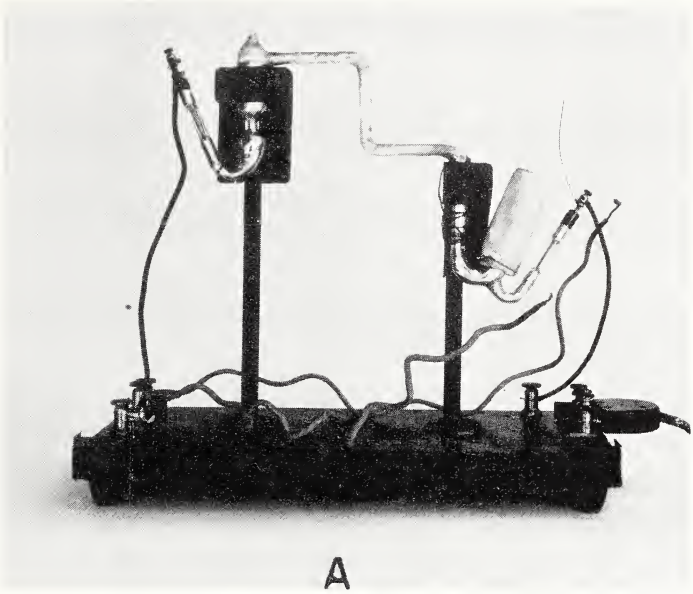
(d) CADMIUM LINES

(1) GENERAL.—The necessity for a number of suitable line sources for polariscopic work has resulted in numerous investigators giving

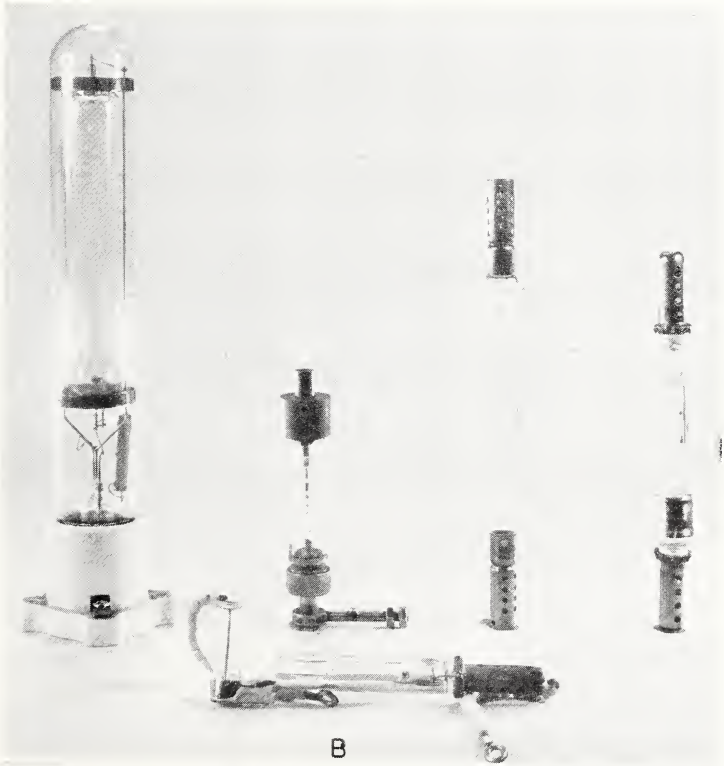
FIGURE 12.—*Mercury vapor lamps.*

A, Shows the original quartz Heraeus lamp first shown in this country at the St. Louis Exposition in 1902. It is still in good operating condition.

B, Shows a group of modern mercury-vapor lamps. In the foreground is a horizontal 110-volt direct-current Uviarc burner; on the extreme right is the same type designed for operation in the vertical position; on the extreme left is a 400-watt alternating-current lamp in glass, which is almost as satisfactory for polariscopic work as the more expensive quartz burners. In the middle are the 1,000-watt, water-cooled, high-pressure quartz capillary lamp (left) and the new 600-watt alternating-current type Uviarc employing only a slight amount of mercury, all of which is vaporized in operation [34].



A



B

See legend on opposite page.

much time to the subject. So far as possible, it is desirable that the lines utilized be uniformly distributed throughout the visible spectrum.

Lowry [35] has suggested the following (given in angstroms): Lithium, 6708, red; cadmium, 6438, red; sodium, 5893, yellow; mercury, 5461, green; cadmium, 5086, green; cadmium, 4800, blue; mercury, 4539, violet. 6708 and 5893 were obtained from flame spectra, and 5461 and 4359 from the quartz-mercury lamp. The cadmium lines 6438, 5086, and 4800 Lowry suggests be obtained from a rotating arc. The electrodes must rotate in opposite directions at a speed sufficiently high to prevent flickering. As electrodes, he uses an alloy of 28 percent of cadmium and 72 percent of silver. The melting point is 860° C. This method has been used at this Bureau and is capable of giving excellent results. The rotating arc is, however, rather difficult to manipulate. Some of the silver lines, namely 5469,

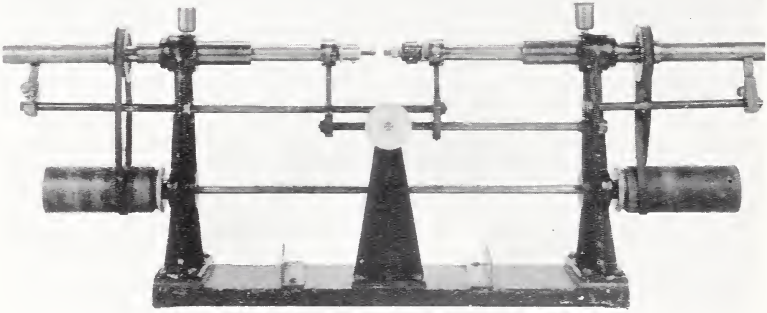


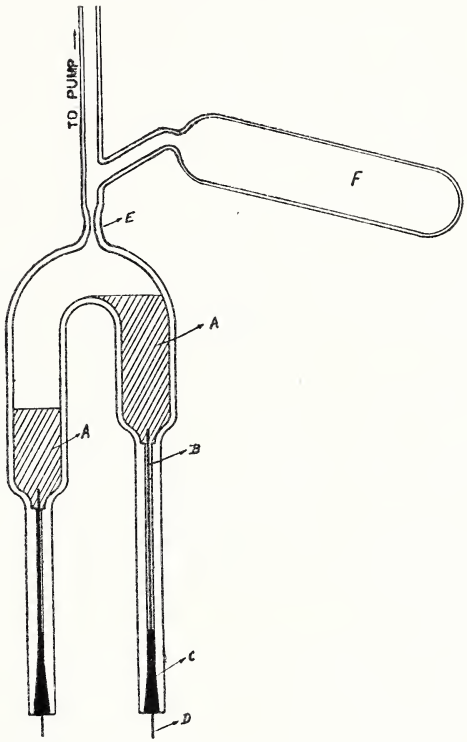
FIGURE 13.—*Rotating arc* (Cd–Ag).

5209, and 4208, may be obtained in this manner also, and with sufficient intensity for polarimetric measurements.

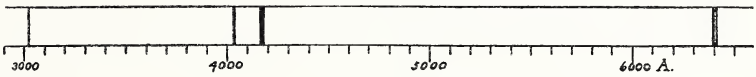
(2) BATES CADMIUM-GALLIUM LAMP [36].—In order to improve the cadmium source, this Bureau has developed a vacuum type of cadmium arc. If pure cadmium is used in a quartz lamp, the adhesion between the cadmium and the quartz results in the destruction of the lamp upon the solidification and cooling of the cadmium. If the cadmium is mixed with mercury to make a soft alloy, the cracking of the lamp is effectively prevented, but the mercury vapor then carries most of the current, since the vapor pressure of mercury is much greater than that of cadmium.

On the other hand, gallium although melting at about 30° C, boils at a very high temperature, approximately 1,500° C. Its vapor pressure is therefore negligible in comparison to that of cadmium. Furthermore, the addition of a few drops of gallium to 10 or 15 ml of cadmium is found to change completely the texture of the latter, rendering it relatively soft and greatly reducing its tensile strength. Subsequently, it was discovered that upon distilling the cadmium from the alloy at a pressure of about 0.001 mm of mercury, the minute quantity of gallium carried over was sufficient to change completely the character of the cadmium and to prevent adhesion between the cadmium and the walls of the lamp. The type of lamp usually used is shown in figure 14.

The total volume of the lamp was approximately 10 ml. The electrodes consisted of tungsten wires, *B*, entering through quartz capillaries. These were closed with seals similar to the type described



A



B

FIGURE 14.—A, *Bates type of cadmium-gallium arc;* B, *gallium spectrum.*

A, Cadmium-gallium alloy; *B*, tungsten electrode; *C*, lead seal; *D*, tungsten lead wire; *E*, capillary for sealing off lamp from pump.

by Sand [37], and later by quartz-Pyrex-tungsten seals when these became available.

In filling the lamp, cadmium containing 2 or 3 percent of gallium, is placed in the side tube, *F*, and distilled under a vacuum of 0.001 mm Hg, or better. When carefully prepared, the lamp will have an indefinite life. One of this type has been in intermittent use for several years and shows no sign of deterioration. The lamp may be

started by heating with a flame to vaporize the metal. It will operate with as little as 3 amperes and a corresponding drop of 14 volts across the lamp, but most satisfactory results were secured with a current of about 7 amperes and a drop of about 25 volts across the lamp. It may be connected directly to a 110-volt direct-current power line through a suitable resistor. Under these conditions a practically pure cadmium spectrum of great brilliancy is obtained. There are no gallium lines to interfere between 4200 and 6400 A, and the ones that do occur are so faint as to be wholly negligible in polarimetric work.

(e) LITHIUM FLAME

The lithium red line ($\lambda = 6708$A) may be obtained in satisfactory intensity by blowing lithium carbonate dust into an oxyhydrogen

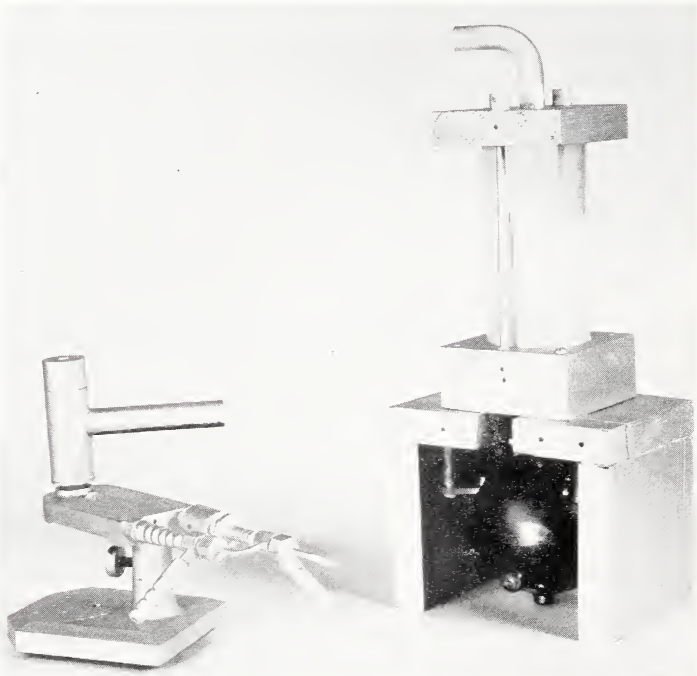


FIGURE 15.—*National Bureau of Standards apparatus for obtaining the lithium flame.*

flame. Apparatus devised for this purpose is shown in figure 15. It consists essentially of a cylindrical glass container, at the bottom of which is a small fan driven by a motor. Lithium carbonate, together with a small quantity of Ottawa sand, is placed in the apparatus. The sand, which is picked up and kept in violent motion by the fan, keeps the carbonate from packing and acts as a sand blast, grinding the carbonate finer and finer the longer it is operated. A slow stream of dried air enters at the bottom and leaves at the top, laden with lithium carbonate dust, whence it is conducted by a rubber tube to the housing around the oxyhydrogen burner.

(f) REMARKS ON PURITY OF LIGHT

In most instances absorption filters do not accomplish sufficient purification. For work even approaching precision, spectral purification needs to be used even with those sources which produce line spectra. The purity of the light used for making rotation measurements has not in the past had the attention which is due it.

If one measures a normal quartz control plate, for instance, with first one and then the other of the two *D* lines ($\lambda = 5896$ and 5890 *A*), which constitute the sodium doublet, a difference of about 0.08° is obtained. Using a good polariscope rotation measurements can be made with a precision of about 0.003 circular degree; while even the smaller instruments yield a precision of about 0.01°. It is obvious, therefore, that a monochromaticity approaching 1 angstrom unit is required even for ordinary work, and a considerably greater degree of purity for precision work, if the uncertainty in the rotation because of wave-length errors is to be reduced to the same order of magnitude as the experimental error involved in making the settings on the scale (matching the field) of the polariscope.

3. QUARTZ CONTROL PLATES

Quartz control plates are plates of crystalline quartz designed to be used as standards of rotation to facilitate precise saccharimetric and polarimetric measurements. They are indispensable in standardizing saccharimeter scales, and also in controlling saccharimetric and polarimetric measurements in the field, by checking the over-all accuracy of saccharimeter or polarimeter at the time the measurements are being made.

Inasmuch as the highest possible precision is frequently called for in polarimetric measurements, quartz control plates must be designed, constructed, and standardized in a manner commensurate with necessary accuracy and dependability.

(a) REQUIREMENTS AND METHODS OF TESTING

(1) Crystalline Purity.—First among the requirements is that of purity; the plate must be of optically homogeneous quartz and contain no striae, inclusions, twinning, or other flaws, which might render the plate unreliable in service. Such flaws, even if not within the effective aperture, i. e., flaws which occur only around the edges covered by the mounting, are not permissible, since the changes in temperature may cause differential expansion and set up strains in the plate, which might make it of doubtful utility.

Plates are tested for purity by placing them between large accurately crossed nicols in a darkened room, using an intense white-light source and compensating for the rotation of the plate by means of a quartz compensating-wedge system. Flaws may best be detected by focusing the observing telescope sharply upon the plate and then rotating the plate in its own plane. Any flaw in the plate will be seen to move with the plate, and hence will be readily detected. With proper technique, this can be made an exceedingly delicate test.

(2) Planeness and Parallelism of the Faces.—A second requirement is that the faces of the plate shall be both plane and parallel to a sufficient degree of precision; otherwise the plate would

be of different thicknesses at different points throughout the free opening, which would give a nonuniform field. At some points the plate, being thinner or thicker, would have less or more rotation than at other points.

Since a standard should be at least as accurate, and preferably more so, than the instrument it is to control, or check, and since the best modern saccharimeters are capable of approaching an accuracy of 0.01° S, it is necessary that quartz control plates do not differ in thickness at any point within the free aperture by more than an amount corresponding to about 0.01° S. Since a 100° plate is 1.59 mm thick, 0.01° S corresponds to a thickness of 0.000159 mm, or between one-fourth and one-third wave length in air of the light usually used in testing them.

The planeness of the faces can be tested most conveniently by observing the interference pattern formed, by reflections from the surface being tested, and from an optical flat. Either a mercury or a sodium light source is satisfactory for the purpose.

The parallelism of the faces is most easily checked by observing the Haidinger rings formed by reflections from the two surfaces of the plate.

Both of these methods as applied to quartz control plates are described in detail by Brodhun and Schönrock [38].

(3) Axis Error.—It is important that the faces of the plate be accurately oriented at 90° to the crystallographic axis, i. e., when in use the light shall pass through the plate in a direction parallel to the principal or crystallographic axis of the quartz crystal. The accuracy of the construction of the plate in this respect is checked by observing the amount of displacement of the uniaxial interference figure when the plate is rotated in its own plane. This scheme was used by Gumlich [39] and later perfected by Schönrock [40], and by Brodhun and Schönrock [38]. The latter designed a special instrument for the purpose, which was built by Schmidt & Haensch and also by R. Fuess. The method is capable of a precision of a few seconds of arc, which is more than is needed, since the tolerance permitted between the crystallographic axis and the normal to the faces of the plate is 12 minutes of arc.

(4) Mounting.—Another factor of great importance, and one that in the past has not been given the attention it deserves, is that of the mounting. The plate should be mounted loosely in a metal frame, the axis of which forms an angle of 90° with the plate. The amount of play between the faces of the plate and the frame should be as small as possible, but the metal should exert no pressure upon the plate under any conditions.

A little play around the circumference of the plate does no harm and is desirable in checking whether the plate is free from pressure and yet has not too much play. One of the most sensitive and re-

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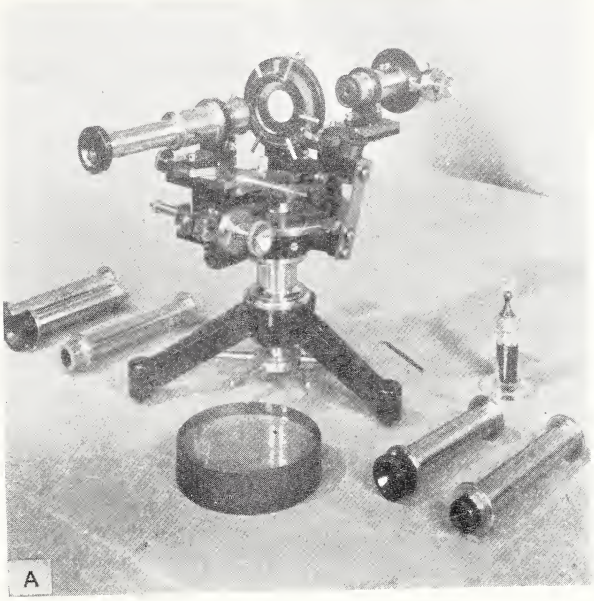
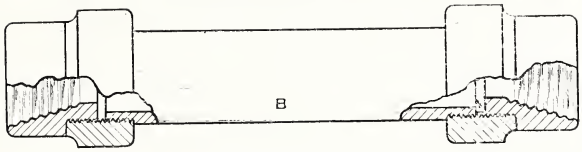
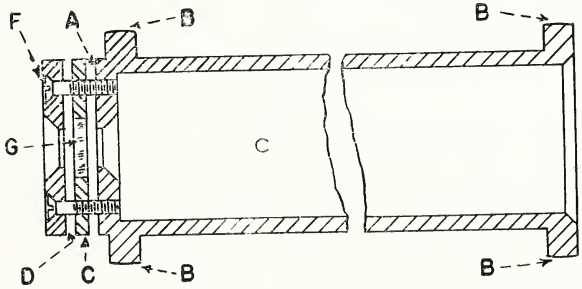
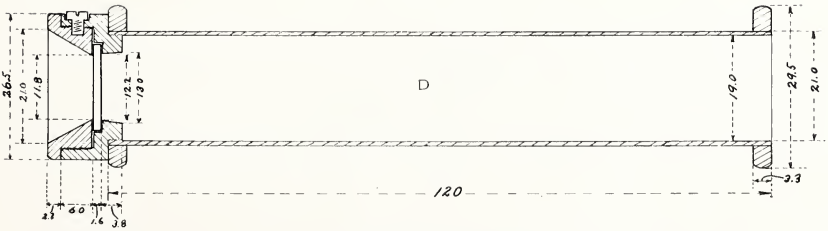
Figure 16.—*A, Axis-error apparatus for testing quartz control plates, and group of mounted quartz plates and the optical flat used for testing the faces for planeness; B, Bausch & Lomb type of mount; C, Hilger type of mount; (The steel ring, C, which carries the quartz plate, G, is ground parallel and lapped down until it is just 0.00015 inch thicker than the plate. It is held in place against the flat surfaces, A and D, by the screws, F. The shoulder, B, rests in the trough of the instrument in the usual manner.); D, Physikalische-Technische Reichsanstalt type of mount (dimensions in millimeters).*









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liable tests is made by ear in a place free from disturbing noises. If the plate is placed close to the ear and shaken sharply in a direction parallel to the axis of the plate, no click should be heard, or at most only a very faint one. A shake parallel to the faces should produce a decided click, proving that the plate is not bound in position by pressure.

(5) Measurement of Rotation.—Inasmuch as precision work of the highest type is frequently called for in meeting the demands for accuracy in standardizing quartz control plates, the mercury line, $\lambda=5461$ A, for the reasons previously outlined, is used exclusively.

Temperature coefficient.—In order to utilize this source to best advantage, the temperature coefficient, α, of quartz for this wave length ($\lambda=5461$ A) and also the constant $\phi_{\lambda=5892}/\phi_{\lambda=5461}$ where ϕ is the rotation, were determined. It was thought advisable to measure α for this wave length, although Lang [41], Sohncke [42], and Le Chatelier [43] state that it has the same value for all wave lengths.
We have

$$\phi_t=\phi_0\ (1+\alpha t),$$

where ϕ_t is the rotation at temperature t and ϕ_0 at zero. For any other temperature, t_1, we have

$$\phi_{t_1}=\phi_0\ (1+\alpha t_1).$$

Hence

$$\alpha=\frac{\phi_{t_1}-\phi_t}{\phi_t t_1-\phi_{t_1} t}.$$

The measurements [24] were made with the most improved types of apparatus. By computing α from the value of ϕ at temperatures between 4° and 50° C, the value obtained was $\alpha=0.000144$. Then between 4° and 50° C

$$\phi_t=\phi_0\ (1+0.000144t). \tag{13}$$

Conversion factor.—In measuring $\phi_{\lambda=5892.5}/\phi_{\lambda=5461}$, a large number of determinations were made, practically all of which were concordant. However, in order to eliminate the personal equation and avoid, as far as possible, errors due to the character of the sodium source, the value of ϕ is computed from the measurements of five plates whose sodium values have been determined at the Physikalisch-Technische Reichsanstalt. The mean of these values and those of this Bureau was taken as the rotation for $\lambda=5892.5$. The rotations were measured in part with a sensitive-strip polarizing system. The greater number, however, were made with an exceptionally good Lippich system. The average value obtained was

$$\frac{\phi_{\lambda=5892.5}}{\phi_{\lambda=5461}}=0.85085. \tag{14}$$

Thus any quartz rotation for the wave length 5892.5 may be obtained by measuring the rotation for the wave length 5461A and multiplying it by the constant 0.85085. By this method the errors due to the character of the sodium source of light are eliminated, and the measurements of one observer may be readily compared with those of another. National Bureau of Standards certificates show the rotation in circular degrees at 20° C for wave lengths $\lambda=5461$ and $\lambda=5892.5$ A. The latter is the so-called optical center of gravity of the two sodium D_1 and D_2.

Measurement.—In carrying out the rotation measurement, the plate is placed in the air bath of the circular-scale polariscope described on page 46, and the optical rotation carefully measured at 20° C for spectrally purified mercury light of wave length 5461 A. In order to eliminate accidental errors as far as practible, at least three sets of readings are made on different days. Moreover, all readings are compared to, and corrected by readings on a set of standard plates which this Bureau maintains as its primary standards. Because of the refinements in the method of checking quartz control plates, it is believed that the sugar values certified are not in error by more than 0. 01°S, or at most 0. 02°S. Repeated determinations made several years apart seldom differ by more than this amount.

(b) NATIONAL BUREAU OF STANDARDS SPECIFICATIONS

In line with the requirements cited above, this Bureau has drawn up the following specifications for quartz control plates:

(1) Purity.—The plate shall be made of quartz which is optically homogeneous, i.e., it shall be free from twinning, striae, strain, and other optical defects.

(2) Planeness, Parallelism.—The faces of the plate shall be both plane and parallel within the following limits: There shall be no departure from true flatness by more than that corresponding to one-half wave length in air of sodium light anywhere within the free aperture of the plate, nor shall there be a radius of curvature of less than 100 m. The plate shall not differ in thickness between any points comprised within the free aperture by more than 0.00015 mm. This thickness corresponds to 0.01°S.

(3) Axis Error.—The faces of the plate shall be accurately orientated at right angles with respect to the crystallographic axis. The axis error, i.e., the angle between the normal to the faces and the crystallographic axis, should be as small as possible and shall not exceed 10 or 12 minutes of arc.

(4) Mounting.—The plate shall be mounted loosely in a metal frame, the axis of which forms an angle of 90° with the faces of the plate. The amount of play between the plate and its surrounding frame shall be as small as possible in the direction parallel to the axis of the plate, but the metal shall exert no pressure upon the plate.

(5) Dimensions.—The plates should be 15 to 17 mm in diameter and, after mounting, should have a free aperture not less than 10 mm in diameter. Plates having low sugar values may be, and it is recommended that they be, composed of two thicker plates, one right-rotating and one left-rotating, mounted in separate mounts of the same type, preferably one on each end of the tube.

(c) SPECIFICATIONS OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS FOR QUARTZ CONTROL PLATES

The following resolutions were adopted by the International Commission for Uniform Methods of Sugar Analysis at its Eighth Session at Amsterdam in 1932:

1. Quality tests of saccharimeter quartz control plates.

(*a*) *Optical purity.*—At least the central 9 mm of the plate must be sufficiently optically homogeneous. Especially plates from 90° to 102°S must not show any

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striae. During the purity test, the plate should be rotated in its own plane at least 360° (about its own axis).

(*b*) *Plane parallelism.*—In general the wedge angle between the faces may at most amount to not more than 20 seconds. For plates between 90° and 102°S this limit must be 10 seconds. The radius of curvature of each of the faces shall be not less than 50 meters.

(*c*) *The axis error,* that is, the angle between the optical axis and the normal to the plate, may at the highest amount to 10 minutes of arc.

2. *Dimensions of the plates.*—The plates must be between 15.0 and 17.0 mm in diameter. After mounting they must have a free aperture at least 10 mm in diameter. Plates having values below ±24°S should be composed of two thicker plates, one plus and one minus, the combined thickness of which, however, must be less than 1.6 mm. The edges of the plates shall be slightly beveled.

3. *Identification marks.*—Near the edge of the plate shall be engraved "IP" (International Plate), the number of the plate, and the year.

4. *Plate mountings.*—It is proposed to accept the form of mounting prescribed by the Physikalisch-Technische-Reichsanstalt wherein the plate is free from pressure, but the clearance is a minimum. For plates below ±24°S, the two plates are to be mounted in separate mounts of the same type, one on each end of the holder tube.

5. *Rotation measurement.*—The rotation in circular degrees shall be made at 20°C, using spectrally purified light either of wave length 5461 or 5892.5 A, obtained, respectively, from a mercury vapor arc of suitable design, or from a sodium light source, such as the Pirani or Osram sodium arc lamp.

6. The plates shall be tested in one or more of the four national physical laboratories, viz., National Bureau of Standards, Washington, D. C.; National Physical Laboratory, Teddington, London; the Physikalisch-Technische Reichsanstalt, Charlottenburg, Berlin; and the Laboratoire National, Paris. All details of the tests and measurements shall be left to these four institutions.

At the Ninth Session at London in 1936, the Referee on Quartz Control Plates made the following recommendations which were unanimously adopted by the Commission:

1. The resolution of the Eighth Session shall be amended to read as follows:

(*a*) *Optical purity.*—The central 9 mm at least of the plate must be sufficiently optically homogeneous. It is essential that plates from 90° to 102° S should not show any striae. During the purity test, the plate should be rotated in its own plane at least 360° (about its own axis). It is recommended that the four National Physical Laboratories should investigate tests for fixing a quantitative limit to permissible defects in homogeneity.

(*b*) *Identification marks.*—Near the edge of the plate shall be engraved "I. P." (International Plate), the number of the plate, the year, and the sign of the testing National Physical Laboratory.

(*c*) *Plate mountings.*—The form of mounting to be acceptable for testing shall be such that the plate shall be free from compression and the clearance a minimum. For plates below 24° S, the two plates are to be mounted in separate mounts of the same type, one on each end of the holder tube.

2. The four National Physical Laboratories, viz., National Bureau of Standards, Washington, D. C.; National Physical Laboratory, Teddington, London; the Physikalisch-Technische Reichsanstalt, Charlottenburg, Berlin; and the Laboratoire National, Paris, be requested to collaborate and determine:

(*a*) The rotation of the 100° S plate in circular degrees for the wave length (optical center of gravity) produced by the Osram sodium vapor arc lamp.

(*b*) The rotation in circular degrees for the wave length (optical center of gravity) produced by the Osram sodium vapor arc lamp for plates of the following approximate values, 25, 50, 75, and 100° S. It is suggested that sets of such plates be interchanged between the above laboratories for comparative tests to be made.

(d) CERTIFICATION OF QUARTZ CONTROL PLATES

The usual procedure at this Bureau in testing quartz control plates is:

1. Examination of the mounting to see if the plate is satisfactorily mounted.
2. Examination between crossed nicols as a test of purity.
3. Examination as to planeness and parallelism of the faces.

4. Measurement of the axis error.

If a plate satisfactorily passes these tests, its optical rotation is measured, at 20° C, using spectrally purified light of wave length 5461 A obtained from a mercury arc.

The rotation for $\lambda=5892.5$ A may be obtained by direct measurement, or by multiplying the rotation for the Hg light by 0.85085. The sugar value of the plate is then assigned, based upon either of the two rotations given above. The sugar value is discussed more fully below under "Saccharimeters."

This Bureau reserves the right to reject any plate showing faults which tend to make it unreliable.

(e) SPECIAL TESTS

Additional data upon quartz control plates submitted for test may be had by special arrangement. Standardization for wave lengths other than $\lambda=5461$ A and $\lambda=5892.5$ A will be made, provided the order of accuracy desired is consistent with the intensity and purity of the source available.

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IV. MEASUREMENT OF ROTATION IN SUGAR DEGREES

1. DEVELOPMENT OF THE SACCHARIMETER

(a) HISTORICAL INSTRUMENTS (FIG. 17)

In the development of the saccharimeter there are two factors that have of necessity received most consideration. They are, first, sufficient illumination of the field for average work and, second, the highest obtainable sensitivity consistent with meeting necessary requirements. Because of the rotatory dispersion, or the different rotation for different wave lengths, precise measurement of rotation ordinarily requires the use of a monochromatic light source. This is especially true if the precision attainable by the utilization of the photometric principle as realized in the halfshade is to be obtained. This condition holds in polariscopes designed primarily for absolute measurements of the rotation of the plane of polarization. Unfortunately a simple monochromatic source of sufficient intensity and otherwise suitable for all polarimetric work has never been realized. In order to obviate this difficulty, Soleil, a Parisian optician [1], as early as 1845 invented the first quartz-wedge compensator and applied it to the polariscope of Robiquet, permitting the use of white light illumination and obviating the necessity of using monochromatic light. He used a double quartz wedge so arranged that it was in effect a quartz plate of variable thickness, opposite in rotation to the sugar solution being measured. Since quartz has almost the same rotatory dispersion as sucrose, this device compensated or balanced out the rotation produced by the sugar solution, wave length by wave length, and returned the vibration planes of all the different wave lengths to the original vibration direction common to all before they entered the optically active substance. Since the calibrated wedge is driven across the field until conditions are as they were before the rotating substance was placed in the intrument, rotatory dispersion is practically eliminated and white light may be used.

The absence of light sources of sufficient intensity has always been one of the most potent factors in influencing the design of saccharimeters. The higher limit of the sensitivity has been almost entirely

determined by this factor. Even with the average halfshade angle of 6° to 8° the polarizing and analyzing nicols are practically crossed, so that only a mere fraction of the incident light ever reaches the eye of the observer. If the halfshade angle is decreased in order to increase the accuracy with which observations can be made, the intensity of the light transmitted is rapidly reduced. Thus monochromatic sources are inadequate in intensity when even fairly accurate settings are to be made, unless the active substance whose rotation is to be measured is quite transparent. Unfortunately this is not the case with many of the optically active liquids. This is especially true of the average raw sugar solution, and hence Soleil, as stated above, invented the quartz-wedge compensator which permits the use of white light with its relatively great intensity.

(b) MODERN INSTRUMENTS (FIG. 17)

The practical necessity for using white light has resulted in the quartz compensating instrument displacing practically all other types of saccharimeters, as is evidenced by the similarity in the perfected instruments of Fric; Bausch & Lomb; Schmidt & Haensch; Peters; Reichert; and others. This has been brought about despite the fact that the compensating wedge ordinarily prevents the full use of the adjustable halfshade angle of the Lippich polarizing system. Thus, while the best results in the designing of polariscopes for use with a white-light source have so far been obtained by using the Lippich polarizing system and a quartz-wedge compensation, all makes have had the great weakness of an unadjustable halfshade angle, and therefore a fixed sensitivity. Only one value of the halfshade angle can be used, and it must necessarily be large enough to give sufficient light to read, for example, the darkest-colored raw-sugar solutions. When polarizing substances having a small coefficient of light absorption, such as the better grades of sugars, are used, in which case the observer has more light than he needs, he still has available only the low sensitivity which corresponds to that value of the halfshade angle which gives sufficient light to polarize substances with a relatively large coefficient of absorption, such as very dark raw sugars. If then it were possible to retain the quartz compensation and at the same time have the halfshade angle adjustable, an advance in polariscope construction would be made comparable with the invention of the wedge.

The defect due to the lack of adjustable sensitivity on a white-light instrument has been in evidence not only in ordinary use but especially so when the saccharimeter was used for research work. The ordinary quartz compensating polariscope is utilized in practically every chemical laboratory. The highest available precision of the instrument is required in order to meet the demands of routine use. Yet the research investigator also has been compelled to depend upon it. The futility of taking a large number of observations on an instrument sensitive to 0.15 percent and using the average value as good to 0.015 percent is too well known to need discussion here. Nevertheless, the chemist has been compelled to do this because the majority of the research problems involving the use of the polariscope require the measuring of rotations with a precision greater than 0.1 percent. There can be no question that the present status of polarimetry would have been immeasurably advanced had there been a

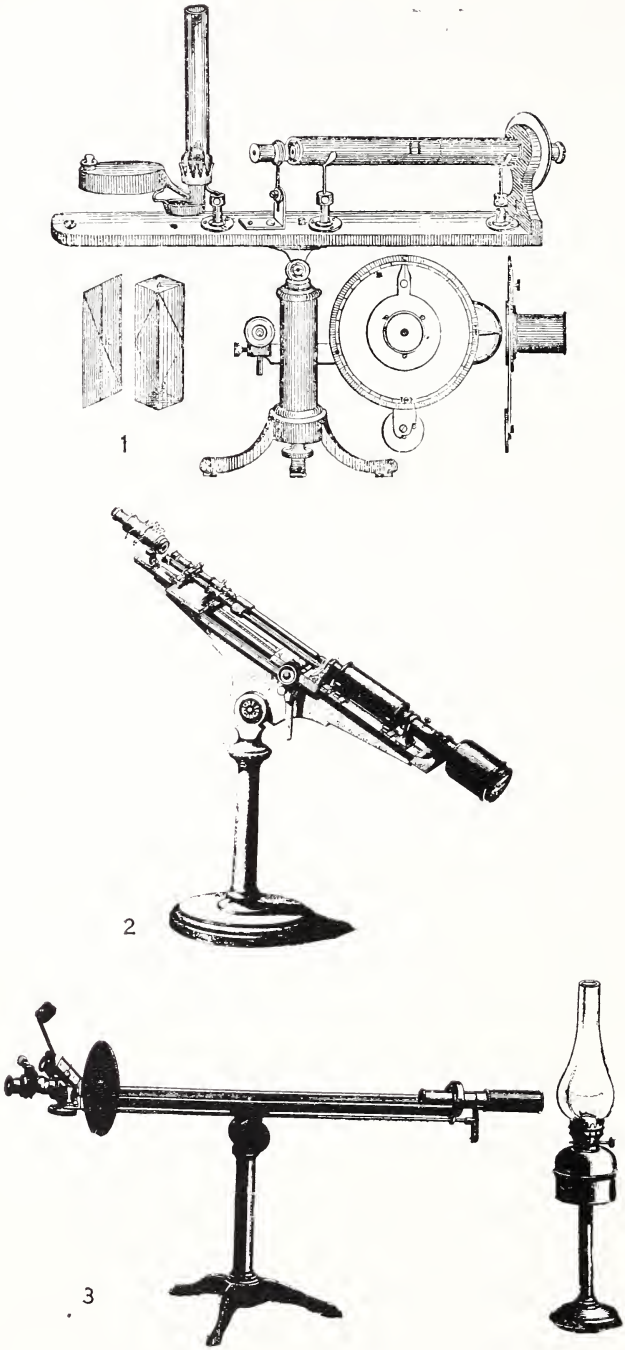


FIGURE 17.—*Old types of saccharimeters.*

1, Ventzke's first modification of Biot's apparatus; 2, Jellet's compensating saccharimeter; and 3, Laurent quartz wedge (Soleil) saccharimeter.

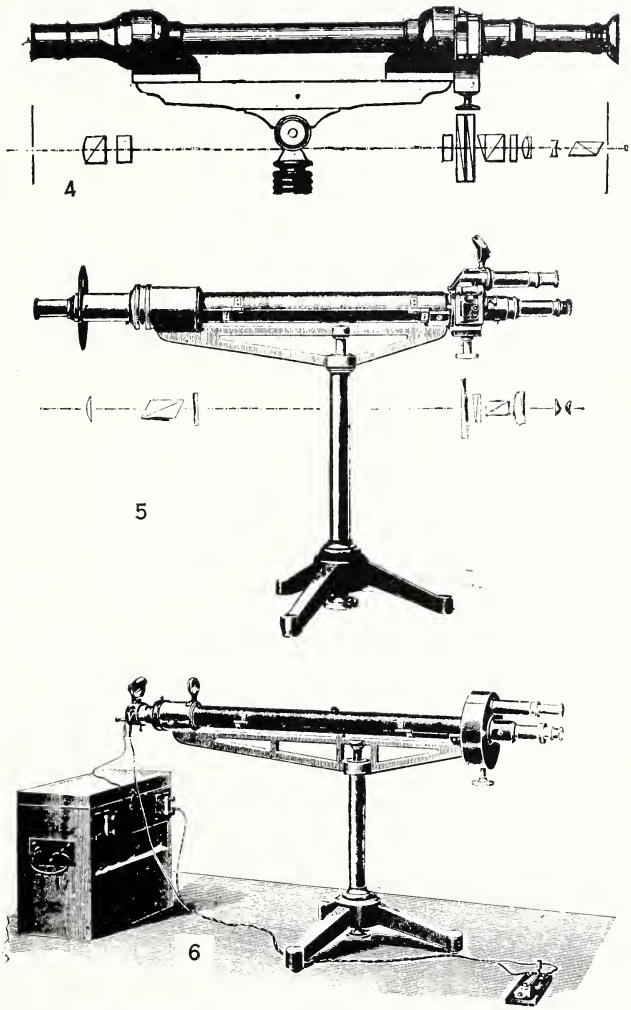
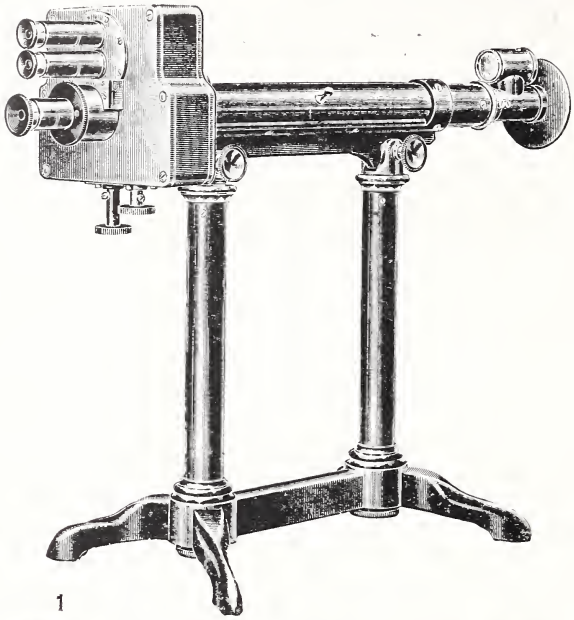


FIGURE 17 (continued.)—*Old types of saccharimeters.*

4, Soleil-Duboscq saccharimeter (sensitive-tint biquartz plate and double quartz-wedge compensator); 5, Schmidt & Haensch type of Soleil saccharimeter; and 6, Schmidt & Haensch type saccharimeter with Jellet-Cornu polarizer.



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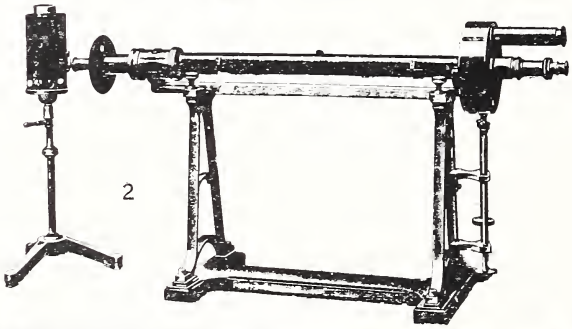

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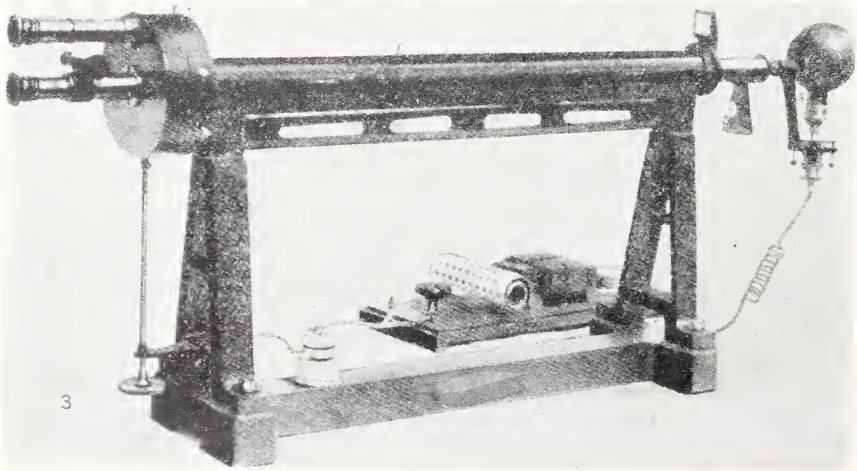

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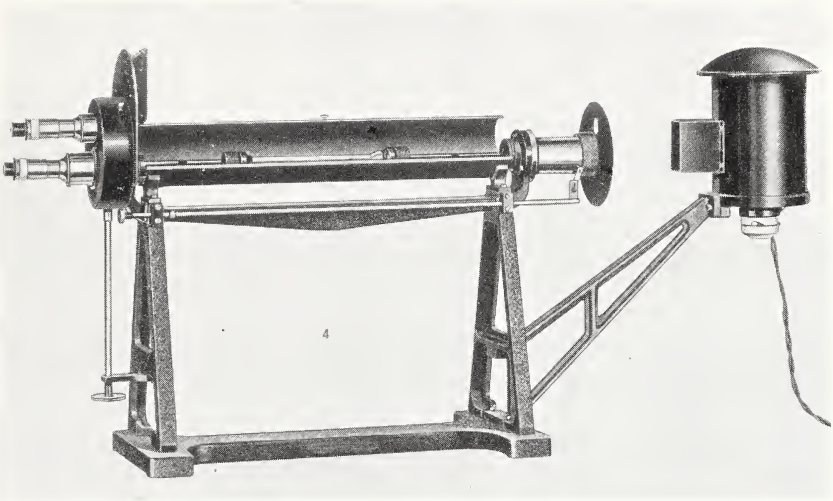
FIGURE 17 (Continued).—*Modern types of saccharimeters.*
1, J. & J. Fric (single wedge); 2, Schmidt & Haensch (Lippich polarizer); and 3, Jobin and Yvon.



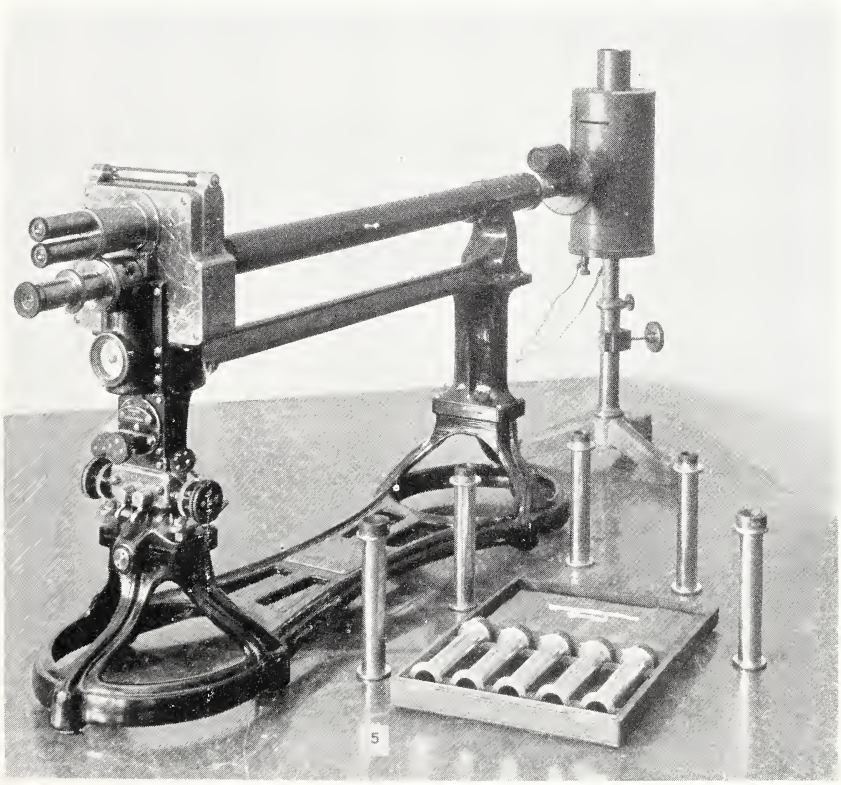


FIGURE 17 (Continued).—*Modern types of saccharimeters.*

4, Bausch & Lomb (American made); 5, Bates type (J. & J. Fric) (adjustable sensitivity type).

saccharimeter capable of being read to 0.01 percent in the hands of chemists at an earlier date.

(c) ADJUSTABLE SENSITIVITY TYPE

In order to build a white-light polariscope with an adjustable sensitivity, the analyzing nicol would have to rotate through a definite angle as the halfshade angle is varied. In such an instrument it is not sufficient that the halfshade angle be merely adjustable, but the far more difficult requirement must be met of having it adjustable without shift of the zero point. This is indispensable for two reasons: first, to permit of making polarizations with the same rapidity as on an ordinary saccharimeter; and second, to eliminate the danger of the observer not properly resetting the analyzing nicol whenever the halfshade angle is changed. The designing of an instrument to meet these requirements would be comparatively simple if the vibration plane of the analyzing nicol bisected the halfshade angle when the halves of the field were matched. In general, the intensities of the light emerging from the large and small nicols of a Lippich system are unequal. Hence when the analyzer is set for a match, its position is different from what it would have been had the beams been of equal intensity. The angular difference, δ, between the two positions of the analyzer was found by Bates [2] to be

$$\delta = \tan^{-1}\left(\tan^3\frac{\alpha}{2}\right) + 0.0103\ \alpha. \tag{15}$$

It is thus evident that if the vibration plane of the analyzer always bisects the halfshade angle, the zero of the instrument will be in error by the angle, δ, and the amount of the error depends on the halfshade angle, α. The zero error, δ, is much smaller and more nearly linear with α than had been suspected. Hence in order to have a negligible change in the zero point as the halfshade angle is varied, it should be necessary to make only a slight modification of the ideal gear ratio in which the analyzing nicol always turns through one-half the rotation of the large nicol of the Lippich polarizer.

The instrument shown in figure 18 was designed at the Bureau of Standards in 1907 [2] to fulfill the theoretical conditions mentioned above, and is one of a number built for the Bureau and the United States Customs Service. It was constructed by the firm of Josef & Jan Fric, Prague, and has been brought to a high degree of perfection. It is double quartz-wedge compensating and has a Lippich polarizing system with the highest grade of nicol prisms. The adjustable sensitivity is attained by a simple mechanism which acts to maintain the analyzer in the proper position to keep the two halves of the field at equal intensities, no matter how the halfshade angle may be varied to suit the pleasure of the observer. In order to accomplish this, the vibration plane of the analyzer is constantly maintained at the angle, δ, to a line bisecting the halfshade angle. A constant match of the field results. Messrs. Fric have succeeded in doing this to such a degree of perfection that there is no observable change in the zero point for a halfshade angle range of 2.5° to 15°. The analyzing nicol and the large nicol of the polarizing system are mounted in bearings and driven by gears from a common horizontal connecting rod. The halfshade angle is varied by turning the milled head which is geared to

the end of this rod. The angle of the halfshade angle is indicated on an engraved dial, 3 cm in diameter, which is in constant view of the operator.

Another important improvement [2] has been made in the location of the milled heads which move the quartz wedges. Heretofore polariscope builders have mounted these heads on the ends of vertical rods, thereby forcing the hand and arm of the observer into a cramped and unnatural position while making the setting. It will be observed that the milled heads are at right angles to the customary position, thereby overcoming this objection. The wedges can be instantly clamped rigid at any position of the scale by means of the clamps, *C* and *N*, figure 18, *B*.

Both the right- and left-rotating wedges are of unusual length, and in the present models read from $\pm 15°$ *S* to $\mp 105°$ *S*. Their scales are the regulation type ordinarily used on Fric saccharimeters. With two exceptions, the scale now used by manufacturers generally is of metal and reads by reflected light. Owing to the shortness of the wedge the reading is necessarily made by means of a magnifying telescope. A black line thus usually separates the vernier and the scale proper or may appear with usage. Owing to the fact that the eye must bridge this line and that the edges of the rulings are not sharp, interpolation of the vernier to hundredths is impossible, and in many cases it is very easy to make an error of 0.1° *S*. The Fric scale, which has been in use for some years, is made with the lines etched on glass, which permits of very sharp rulings. What is of even greater advantage, it is read by transmitted light, the black dividing line between the vernier and the scale being thus eliminated. Not only is this scale much easier on the eye of the observer, but it also permits of reading accurately to 0.01° S. It is illuminated by waste light collected by a 45° mirror, located in front of the polarizing system. Thus it is not necessary to have any extraneous light in the room, as all the light needed enters the instrument through the collecting lens in the end of the tube. In investigations utilizing the saccharimeter, where temperature corrections are to be made, it is necessary to know accurately the temperature of the quartz wedges. Polariscope builders do not generally make provision for this. A thermometer (10° to 40° C, in one-fifth degree) with a horizontal scale and with its bulb between the quartz wedges has accordingly been mounted in a brass case on top of the metal housing containing the compensator. For all ordinary sugar testing, where the temperature of the room changes slowly, the reading of the thermometer is practically the temperature of the room. The observer is thus able to take the temperature of the wedges with the same facility that he reads the scale on his instrument, since the thermometer scale is in a similar position and is illuminated by the same light source.

In general, when a tube of liquid is placed in a polariscope, there is present a certain amount of haziness which seems to overlie the field of view. It is due to depolarized light and interferes with the focusing and the accurate matching of the halves of the field. By proper diaphragming, this has been reduced to such a low minimum that it may be said to be practically eliminated. When a tube is placed in the instrument, the observer sees a clear, sharply defined, circular field with no extraneous light. The observing telescope, as well as the two reading telescopes for the scale, has screw adjustments

which permit of accurate and rapid focusing. Still further improvement has resulted from making the base of the instruments exceptionally heavy and mounting it on rubber tips. The resulting inertia of the instrument and friction on its supporting bench prevent accidental shifting with reference to the light source.

A twofold object has been kept constantly in view in designing this instrument: (1) to produce a saccharimeter of great flexibility for regular commercial testing and to correct the defects of the ordinary instrument; (2) to provide the chemist with a white-light instrument

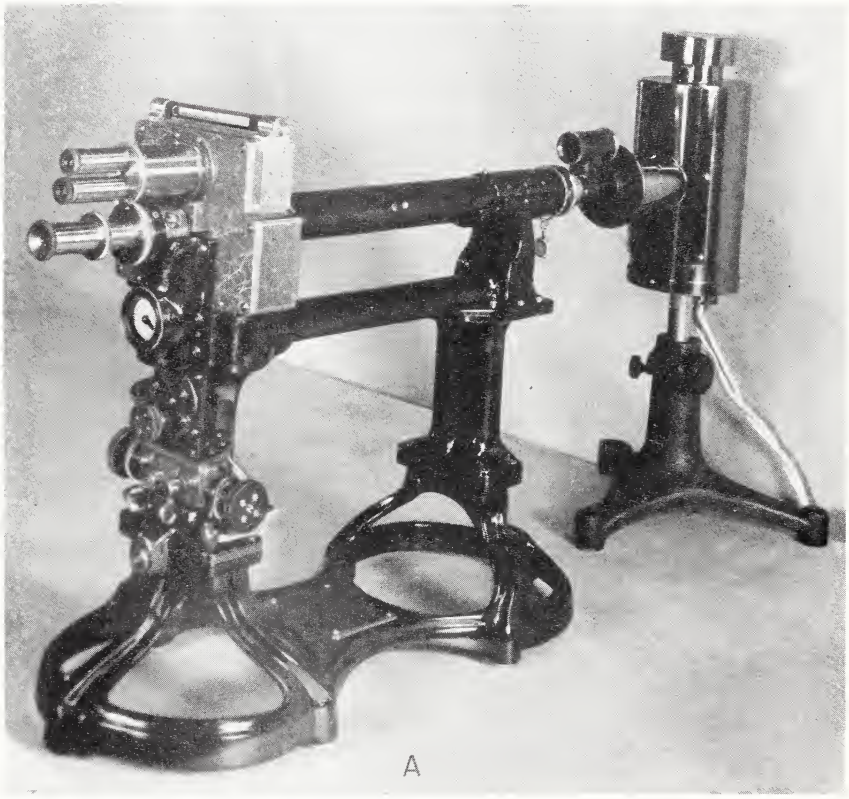


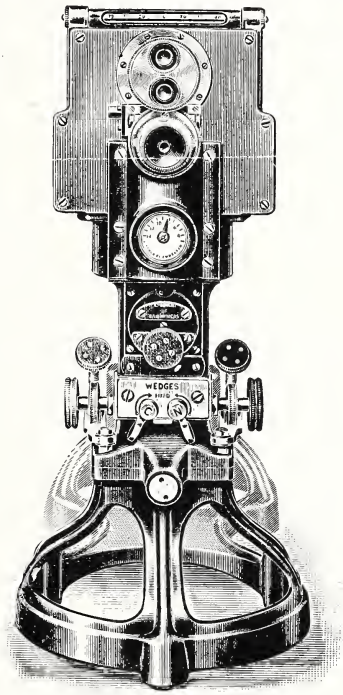
FIGURE 18.—*A, Bates type adjustable-sensitivity saccharimeter with NBS polariscope lamp and bichromate filter.*

suitable for research work. The result has been the production of an instrument of a greater range of adaptability than any saccharimeter heretofore built. In measuring rotations with the greatest possible accuracy, or when it is desired to make the settings with the least possible strain on the eye, the observer has only to change the halfshade angle until he has just sufficient light to bring the two halves of the field to the same intensity, without undue eyestrain. He then has for his eye an instrument so adjusted as to give the maximum sensitivity for making the setting, no matter what the character of the substance whose rotation is being measured.

2. BASIS OF SACCHARIMETER CALIBRATION

The specifications defining the 100° point of saccharimeters have been changed many times since Ventzke [3] defined the normal sugar solution in 1842.

Two markedly different saccharimeter scales are in use today, each purporting to give the correct percentage of sucrose in a sample. They are the French Scale and the International Sugar Scale. The former is used largely in France and the French Colonies; the latter is used generally throughout the rest of the world. The International Sugar Scale is the official scale of the International Commission for



B

FIGURE 18 (Continued)—*B, front view of saccharimeter shown in figure 18, A.*

Uniform Methods of Sugar Analysis and was adopted at the Eighth Session of the Commission in 1932 at Amsterdam. Obviously any saccharimeter scale is, by definition, a basis on which the standardization of the saccharimeter may be brought about. In any consideration of the saccharimeter scale it is essential that there be kept clearly in mind the differentiation between mere definition of the scale and the numerical values of the constants upon which its correctness depends. The confusion which has long existed with regard to saccharimeter scales may be correctly attributed to the use of incorrect values for these constants.

Probably no industrial commodity is so widely utilized in international trade as sucrose and its associated products. Therefore, it is of great importance that there be but one sugar scale, that is, one basis of standardization of saccharimeters in use throughout the world. Such a consummation must ultimately be brought about in view of the importance of the matter to international trade and especially because of the necessity of reporting the results of research workers in unmistakable values. Until this can be done, and under present conditions, it is therefore of special importance, insofar as the inherent characteristics of the French and the International Sugar Scales will permit, that the two scales give results that are in agreement within the experimental error with which saccharimeter measurements can be made. It is fundamental that tests of a sample of sucrose should show an identical sucrose content regardless of the scale used.

The specific rotatory power or specific rotation $[\alpha]$ is, by definition [4], proportional to the rotation divided by the weight per volume, that is,

$$[\alpha]=\text{constant}\times\frac{\text{rotation}}{\text{weight per volume}}=K\frac{\alpha}{c},$$

or more specifically

$$[\alpha]_D^{20}=\frac{100\times\alpha_D^{20}}{c\times l}, \tag{16}$$

where $[\alpha]_D^{20}$ is the specific rotation at 20° C measured with the D line of sodium, α the observed rotation, c the concentration expressed in grams per 100 ml of solution, and l the length in decimeters.

Hence in the formulation of any saccharimeter scale based upon the above equation, some more or less arbitrary choice of value for either one or the other of these two quantities, α and c, must be made before the other can be fixed.

The French chose to let the 100° point of their scale be fixed by a definitely selected rotation, $\alpha=21°40'$, and to determine by experiment, based upon the law stated above, what weight of sugar (which was called the normal weight) was required to produce that rotation.

The Germans, on the other hand, following Ventzke, chose to select a normal weight, c, and determine by experiment what rotation, α, corresponded thereto and to let that rotation fix the 100° point of their scale.

It is clear that in establishing both scales actual physical measurements must be made, both of the weights and of the rotations. It therefore makes no difference in the final analysis whether the weight be considered fundamental and the rotation consequential or whether the rotation be considered fundamental and the weight consequential. In the abstract both lead to the same result, namely a relation or ratio between rotation and weight (per standard volume).

However, practical considerations, such as established usages, choice of values which determine the openness of the scale, effect of concentration on specific rotation, and other factors not involving the fundamental law itself, may operate to make one particular choice of scale preferred over another.

(a) THE FRENCH SUGAR SCALE

It is of interest to recall that the French Sugar Scale was originally based upon the rotation of 1 mm of quartz for sodium light to fix the 100° point. This constant was determined by Broch [5] to be 21°40′ (21.667°) for sodium light. The usual procedure has been to lay off 65° on a circle and divide the 65° segment into 300 equal parts, taking the 100th division mark as the 100° point. Instruments were constructed on this basis, and when it was later found that the rotation for 1 mm of quartz was somewhat higher, the original value (21°40′) was retained in order to avoid confusion of scales. This procedure necessitated the abandonment of the original definition of the 100° point for the French Sugar Scale. The 100° point thus has always been and still is fixed by the absolute rotation, 21°40′. In this sense the French Sugar Scale has never been changed. However, the estimate of the amount of sugar required to produce this rotation, namely the value of the normal weight, has undergone many changes. Over 20 different values have been assigned to the normal weight, ranging from 16.0 to 16.51 g. In 1875 the value of Girard and de Luynes [6], 16.19 g, was adopted as the official weight and remained so for more than 20 years. In 1885 [7] Sidersky called attention to the error in the then official normal weight of 16.19 g, and was criticised for questioning the correctness of the official normal weight [8]. Nevertheless, Sidersky had the courage of his convictions and 11 years later, in 1896, his value was made the official value. This value (16.29 g) was based upon two considerations [8]: (1) A calculation of the normal weight, using Tollens' value, 66.5°, for the specific rotation of sucrose, whereby he obtained the value 16.295 g; and (2) the direct comparison of a Schmidt & Haensch and a Laurent saccharimeter by means of a quartz plate, which he read in both instruments. He assumed that the Schmidt & Haensch instrument was correct, since it was supposed to have been directly calibrated by means of pure sucrose, and calculated the weight which would have to be used with the Laurent instrument to give the correct percentage of sugar. He found for this value 16.30 g, which confirmed his calculated value, 16.295 g. It was not known at that time, as it is now, that the Schmidt & Haensch instruments of those days were in error by about 0.2 percent, the 100° point then corresponding to an absolute rotation of 34.68° instead of 34.620°, as at present. Had this error been known at that time, Sidersky's experiment would have yielded a result of 0.2 percent lower, or 16.27 g. Also, all subsequent determinations of the French normal weight have yielded results slightly lower than 16.29 g.

Following the action of the IIme Congres International de Chimie Appliquée (Paris, 1896) in adopting 16.29 g as the official normal weight for the French Sugar Scale, a commission was appointed for the revision of the saccharimetric normal weight. This commission decided that further experimental work was required in order to establish the normal weight on a firm foundation. This work was undertaken by Mascart and Benard [9] at the Collége de France and also by Pellet [10] at the Sorbonne.

As a result of these experiments the correctness of the value 16.29 g was considered to be amply confirmed. However, it has been recently pointed out [11] that had the values actually found by these observers been used instead of the official value which it was considered they

had corroborated, the French Sugar Scale would from that time on have been in agreement with the International Sugar Scale which was adopted by the International Commission for Uniform Methods of Sugar Analysis at Amsterdam in 1932. Mascart and Benard [9] gave 66.54° as the specific rotation of sucrose, and 16.284 g weighed in vacuo as the normal weight. Through an error in converting this weight in vacuo to weight in air with brass weights, they arrived at the value 16.29, confirming Sidersky's calculation. If this error is eliminated, Mascart and Benard's value becomes 16.27 g.

Also Pellet [10] gave $[\alpha]_D^{20}=66.536$, and 16.285 g in vacuo for the normal weight. The latter corresponds to 16.27 g weighed in air with brass weights.

In 1933, 38 years after his original calculation, Sidersky [8] accepted the specific rotation of 66.54° given by Schönrock [12] as the best average value and again calculated the normal weight and found the value to be 16.282 g. This he said differed by only a negligible amount from 16.29 g. Sidersky appears to have overlooked the fact that the specific rotation calculated from Schönrock's formula, which he accepted, is that based upon weights in vacuo, and hence that the normal weight which he obtained is the normal weight in vacuo. Corrected to weighings in air with brass weights, his figure becomes 16.272 g. If 21.667° be used, instead of 21.67° which Sidersky used, this figure is still further reduced to 16.270 g.

It has also been shown [11] by calculation from the best available constants that a French normal weight of 16.269 g would be necessary to bring the French Sugar Scale and the scale of the International Commission for Uniform Methods of Sugar Analysis into equivalence. This normal weight exactly (considering that the tolerance of experimental error is set at 0.002) equals that calculated by Sidersky, namely 16.270 g, after due attention is paid to the obviously necessary correction for buoyancy of the air and the 100° French Sugar Scale point rotation taken as 21.667°, instead of 21.67°, and also is the same as that actually indicated by the data of both Mascart and Benard and of Pellet.

Since the 100° point of the French Sugar Scale is fixed by definition as a rotation of 21°40′ or 21.667°, it is advisable to use the latter figure to replace the less accurate value of 21.67° now used. Paralleling the definition of the International Sugar Scale, the following statement holds for the corrected French Sugar Scale:

(1) Normal quartz plate=100° French Sugar Scale=21.667 ±0.002° (λ=5892.5 A) at 20° C.

(2) The graduation of the saccharimeter shall be made at 20° C. 16.269 ±0.002 g of sucrose dissolved in water, and the volume made up to 100 ml, all weighings to be made in air with brass weights, the completion of the volume and the polarization to be made at 20° C, on an instrument graduated at 20° C, gives a reading of 100° French Sugar Scale.

Quoting from Bates and Phelps [11]:

> From a consideration of the foregoing it is apparent that many of the difficulties and uncertainties which have been attributed to the French Sugar Scale never had an actual existence. They have arisen through an error in adopting a normal weight which the experimental evidence did not fully justify. It should be a simple procedure to eliminate them. It is therefore suggested that the value 16.269 ±0.002 g weighed in air with brass weights be adopted as the official

normal weight for the French Sugar Scale. When this is done the present official normal weight of 16.29 g will have been discarded. Should this be done, not only will the International Sugar Scale and the French Sugar Scale be brought into exact agreement but there will result a long-overdue recognition of the accuracy of the experimental work of those French investigators whose work was interpreted as providing a value of 16.29 g for the normal weight. It is a fortuitous circumstance that brings the two scales into complete correspondence, and it is worthy of note that these investigators, with the limited facilities available at the early date at which the work was carried out, obtained values for the specific rotation and the normal weight of sucrose identical with those obtained by the use of modern instruments and methods. The adoption of the normal weight, 16.269 g, as the official normal weight for the French Sugar Scale would be an important development of great benefit to the sugar industry of the world.

This has now become an accomplished fact. By an official decision of March 26, 1938, the French Minister of the Budget ratified the change from 16.29 to 16.269 $\pm$0.002 g for the official French normal weight, to be effective September 1, 1938 [13].

(b) THE GERMAN, OR VENTZKE, SCALE

Ventzke [3], in 1842–43, proposed a method for establishing the sugar scale which would make the use of a chemical balance unnecessary. The 100° point of his scale was established by the rotation of a sucrose solution having a specific gravity of 1.100 at 17.5° C referred to water at 17.5° C. However, it was soon found that the specific-gravity method was unsatisfactory in use. Accordingly the weight of sucrose in 100 ml of Ventzke's solution, namely 26.048 g, was taken as the normal weight and the specific-gravity method was abandoned. Many of the old instruments were made for use with 26.048 g in 100 ml.

When the Mohr sugar flask came into general use in 1855, polariscope builders began determining the 100° point by the use of this flask and the same normal weight, 26.048 g, as before, which was of course an entirely different basis, since 100 Mohr cc equals 100.234 ml. Many saccharimeters in use today were constructed on this basis, which may be more fully stated as follows:

The 100° point (Ventzke) is determined by the rotation in a 200-mm tube of a solution containing 26.048 g of sucrose, weighed in air with brass weights, in 100 Mohr cc at 17.5° C, the temperature of the quartz wedges, as well as the polarization temperature, being 17.5° C. From 1855 to 1900 practically all saccharimeters except those using the French Sugar Scale had their 100° points determined on the basis given by this last definition of the Ventzke Scale.

(c) THE INTERNATIONAL SUGAR SCALE

The Ventzke Scale, although in general use for many years, has never been fully understood by polariscopists generally. This has led to much confusion and to the use of 100-ml flasks on instruments standardized for use with the Mohr flask. In addition, 17.5° C is well below the temperature of the average laboratory. Because of these and other considerations, the International Commission for Uniform Methods of Sugar Analysis at the Paris meeting in 1900 recommended the use of a new definition of the 100° point [14], based upon "true cc" and a standard temperature of 20° C. The change to 20° C necessitated a change in the normal weight in order to keep the physical dimensions of the new scale comparable with those

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of the Ventzke Scale. Correcting for the change in the specific rotation (−0.000184), the expansion of a glass tube (+0.000008), quartz wedge (−0.000130), and metal scale (−0.000018), the new weight was calculated to be 26.01+ g. It was thought advisable to ignore the small fraction and use the round number 26.00 as the normal weight, and the Commission officially so decided [14]. Owing to the absence of a more suitable term, and in order to divorce it as completely as possible from confusion with the Ventzke Scale, the new scale was referred to as the International Sugar Scale. The International Sugar Scale then was defined at the Paris meeting as follows: "The graduation of the saccharimeter shall be made at 20° C, 26.00 g of sucrose dissolved in water and the volume made up to 100 metric cc and polarized in a 200-mm tube. All weighings are to be made in air with brass weights, the completion of the volume and the polarization are to be made at 20° C. This will determine the 100° point."

The advantages of the new scale were at once appreciated. It has been adopted by the National Bureau of Standards, the United States Treasury Department, the Physikalisch-Technische Reichsanstalt, the Institut für Zucker-Industrie and also by the makers of saccharimeters.

(1) Herzfeld-Schönrock Version.—Following this meeting of the Commission, Herzfeld [15] and Schönrock [16] (1901–04), on the basis of the above definition of the International Sugar Scale, standardized a number of quartz control plates on the saccharimeter and then measured their optical rotation for sodium light. They found, as the average of 10 plates, that a quartz plate which read 100° on the quartz-wedge saccharimeter with white light, filtered through bichromate, read 34.657° on a circular-scale polariscope for sodium light. This value, 34.657, became known as the Herzfeld-Schönrock conversion factor. By the use of this factor, optical rotations of quartz plates determined with sodium light could be converted into saccharimeter degrees and the standardization of saccharimeters effected without resorting to the use of a pure sucrose solution, which is always difficult to prepare. This version of the International Sugar Scale—namely the one which for all practical purposes had its 100° point set by the rotation in the saccharimeter of a quartz control plate of such thickness that its rotation for sodium light was 34.657—has frequently been referred to as the Herzfeld-Schönrock scale. This scale was the practical formulation of the International Sugar Scale as defined at the meeting in 1900 of the Commission and remained in practically world-wide use for many years.

(2) Bates-Jackson Version.—At the meeting of the International Commission for Uniform Methods of Sugar Analysis in 1912 in New York, Bates reported [17] that work at the National Bureau of Standards indicated that the Herzfeld-Schönrock scale was not quite correct. A committee was appointed to investigate the question and report on it at the next meeting. The war intervened and the scheduled meeting was not held.

In 1916 Bates and Jackson [18] published their work on the redetermination of the 100° point of the saccharimeter, wherein it was shown that a normal solution of pure sucrose read only 99.895° on the Herzfeld-Schönrock scale, and consequently the 100° point should be where the 99.895° point then was, and that the corresponding quartz control plate read 34.620 for sodium light and 40.690 for mercury green. Because there seemed little likelihood, due to international

conditions, that the Commission would again meet for some time to come, the values found by Bates and Jackson were officially adopted by the National Bureau of Standards and the United States Treasury Department without waiting for the reconvening of the Commission, and were used in all of their subsequent work. Their lead was followed by makers of saccharimeters and by others generally throughout the sugar world. This version of the International Sugar Scale became widely known as the Bates-Jackson scale. The publication of this work stimulated great activity in the field, and although its validity was at first questioned in certain quarters, yet later, as more and more data were accumulated by world-wide investigators, it was found to be correct. In fact, when the Commission finally met in 1932 in Amsterdam [19], after a lapse of 20 years, it was found that the average of all the values determined by investigators of international prominence working in various parts of the world was exactly that found by Bates and Jackson and reported in 1916.

(3) Amsterdam Version (1932) [19].—At this meeting in 1932 the Commission adopted, under subject 1, the following resolutions:

(a) It is recommended that this Commission adopt a standard scale for the saccharimeter and that this scale be known as the "International Sugar Scale." Rotations expressed in this scale shall be designated as degrees sugar (° S).

(b) It is recommended that the polarization of the normal solution (26.000 g of pure sucrose dissolved in 100 ml, and polarized at 20° C in a 200-mm tube, using white light and the dichromate filter as defined by the Commission) be accepted as the basis of calibration of the 100° point on the International Sugar Scale.

(c) It is recommended that the reading of the normal sugar solution on the Herzfeld-Schönrock Scale be accepted as 99.90° S.

(d) It is recommended that the following rotations shall hold for the normal quartz plate of the International Sugar Scale:

$$\left.\begin{array}{c}\text{Normal Quartz Plate}=100^\circ\ \text{S}=40.690^\circ\pm0.002\ (\lambda=5461\ \text{A})\ \text{at}\ 20^\circ\ \text{C.}\\ 1^\circ\ (\lambda=5461\ \text{A})=2.4576^\circ\ \text{S.}\end{array}\right\}(17)$$

$$\left.\begin{array}{c}\text{Normal Quartz Plate}=100^\circ\ \text{S}=34.620^\circ\pm0.002\ (\lambda=5892.5\ \text{A})\ \text{at}\ 20^\circ\ \text{C.}\\ 1^\circ\ (\lambda=5892.5\ \text{A})=2.8885^\circ\ \text{S.}\end{array}\right\}(18)$$

(e) It is recommended that the Commission suggest that new saccharimeters be graduated in accordance with the International Sugar Scale and be inscribed by the manufacturers with the phrase, "International Sugar Scale." In the case of existing instruments graduated on the Herzfeld-Schönrock scale, it shall be permitted either to change the saccharimeter scale or to use a weight of 26.026 g in 100 ml.

(f) It is recommended that the method of purification of sucrose for use in fixing the 100° point on the saccharimeter scale, which was adopted at the Paris session of the Commission (in 1900), be subjected to further study.

(g) It is proposed that the recommendations (a) to (e) shall come into effect on September 1st, 1933.

At first reading it might appear that (b), (c), and (d) are three different definitions of the 100° point which might or might not be concordant. A little consideration, however, will show that (b) is a general restatement of the fundamental basis of the saccharimeter scale, while (c) is a recognition of the essential correctness of a particular numerical value which had been arrived at through the application of the general definitions of (b) to the then existing sugar scale. (c) thus transfers the general definition (b) to the actual physical instruments used for sugar testing and is the concrete physical expression, as determined by experiment, of the fundamental definition given in (b).

In (d) there is set up an equivalent secondary or working standard, based upon the numerical value in (c), whereby saccharimeter scales may be checked or standardized without recourse to the difficult procedure of preparing and using a normal solution of pure sucrose.

In fact, having once determined the correct quartz control-plate equivalent (conversion factor), the original definition of the saccharimetric scale could be lost or discarded without affecting the graduation or standardization of saccharimeters. The 100° point could at any time be set or checked by the simple expedient of using a quartz control plate whose absolute rotation is 34.620° for sodium light or 40.690° for mercury light of wave length 5461 A. Since the values of such plates are not subject to change, they are far more convenient for the calibration and checking of saccharimeter scales than the normal solution of sucrose.

It is thus seen that (d) is the practical expression of (b) and (c) in terms of the absolute rotation of a quartz control plate and supplies the means whereby saccharimeter scales may be readily duplicated or checked.

(4) Correction of Saccharimeters to the International Sugar Scale.—In Resolution 1(e) adopted by the International Commission for Uniform Methods of Sugar Analysis in 1932 in regard to the method of correcting saccharimeters to the new scale [19], two alternatives are provided: (1) ". . . it shall be permitted either to change the saccharimeter scale or" (2) "to use a weight of 26.026 g in 100 ml." The second alternative, namely changing the normal weight by a slight amount, is objectionable from the standpoint of introducing additional complications and is therefore to be discouraged.

The first alternative is much to be preferred, namely to change the saccharimeter scale. This does not mean that the existing scale must be removed and regraduated or replaced. It is sufficient to change the scale by the simple procedure of recalibrating it in terms of the desired scale by the use of standardized (International Sugar Scale) quartz control plates and applying the small scale corrections so obtained to all polarizations made in the subsequent use of the instrument. It is worthy of note that scale corrections resulting from inaccuracies in the wedges and other optical parts, including residual inaccuracies in the scale itself, may in many instances be nearly as large as the corrections referred to above and for accurate work must be taken into account either by the use of a calibration table or chart or by the use of a standard quartz control plate. No additional inconvenience is involved, therefore, if the corrections due to change of scale are included with those due to residual inaccuracies in the construction of the instrument.

3. ADDITIONAL CONSTANTS OF THE QUARTZ-WEDGE SACCHARIMETER

(a) ROTATION RATIOS FOR QUARTZ AND SUCROSE SOLUTIONS

The ratios of the rotations in circular degrees of quartz and of sucrose solutions for two wave lengths have been determined as follows: [18]

$$\text{For quartz } \frac{\phi^{20}{}_{\lambda=5892.5\text{ A}}}{\phi^{20}{}_{\lambda=5461\text{ A}}}=0.85085 \qquad (19)$$

$$\text{and for sugar } \frac{\phi^{20}_{\lambda=5892.5\text{ A}}}{\phi^{20}_{\lambda=5461\text{ A}}}=0.84922 \qquad (20)$$

(b) ABSOLUTE ROTATION OF NORMAL SUCROSE SOLUTION

The rotation of the normal sugar solution for $\lambda=5461$ A was found by direct measurement.

$$\text{Normal sugar solution}=100^\circ \text{ sugar}=40.763^\circ. \qquad (21)$$

Since the rotation ratio for the normal solution for $\lambda=5892.5$ A and $\lambda=5461$ A is shown by eq 20 to be 0.84922, the rotation of the normal solution for $\lambda=5892.5$ A is

$$\text{Normal sugar solution}=100^\circ \text{ sugar}=34.617^\circ. \qquad (22)$$

(c) ROTATORY DISPERSION CURVES OF QUARTZ AND NORMAL SUCROSE SOLUTION

The difference between the rotations of the normal quartz plate and the normal solution for $\lambda=5892.5$ A is shown to be 0.003° and for $\lambda=5461$ A 0.073°. The values indicate that the rotatory dispersion curves of plate and solution cross at about $\lambda=5850$ A. The reading of the normal solution on the true saccharimeter scale with the source $\lambda=5892.5$ A has been calculated to be 99.99°S.

(d) ROTATION DIFFERENCE, IN SUGAR DEGREES, FOR NORMAL SUCROSE SOLUTION BETWEEN $\lambda=5461$ A AND $\lambda=5892.5$ A

The difference in rotation in sugar degrees, for the normal solution on the saccharimeter, for the sources $\lambda=5461$ A and $\lambda=5892.5$ A, was calculated from the absolute rotations, with the following result:

$$\text{Saccharimeter reading } (\lambda=5461\text{ A})-\text{saccharimeter reading } (\lambda=5892.5\text{ A})=0.19_2\text{S}. \qquad (23)$$

An independent experimental determination was made of this difference and the value 0.18_5° obtained.

(e) THICKNESS OF THE NORMAL QUARTZ PLATE

Inasmuch as the value of the conversion factor, i. e., the rotation of the normal quartz plate, is found to be 34.620° for $\lambda=5892.5$ A and 40.690° for $\lambda=5461$ A, the old value of 1.5958 mm for the thickness of the normal plate is no longer applicable. Gumlich [20], as the result of a painstaking investigation, found the rotation of 1 mm of quartz for $\lambda=5892.5$ A (the light traveling parallel to the optic axis) to be 21.7182°$\pm$0.0005 at 20° C. Recently Lowry [21, 22] has made a number of measurements on the rotation of quartz and finds at 20° C 21.7283° per mm for ($\lambda=5892.5$ A) and 25.5371° per mm for $\lambda=5461$ A. The values of the thickness of the normal plate calculated from the above data are given in table 4. The argeement between the second and third values in column 4 is very satisfactory in view of the fact that two independent values of the rotation per millimeter are used. The agreement between Gumlich's and Lowry's values for sodium light is not satisfactory.

TABLE 4.—*Thickness of the normal quartz plate*

Wave length of light source	Rotation of normal plate	Rotation of 1 mm of quartz at 20° C; light parallel to optic axis	Thickness of normal plate
1	2	3	4
A			*mm*
5892.5	34.620° (Bates and Jackson)	21.7182° (Gumlich)	1.5940
5892.5	34.620° (Bates and Jackson)	21.7283° (Lowry)	1.5934
5461.	40.690° (Bates and Jackson)	25.5371° (Lowry)	1.5934

(f) SPECIFIC ROTATION OF SUCROSE

Of all the polarimetric constants relating to the sugars, none has received the thorough study by numerous investigators that has been given to the specific rotation of sucrose and its variations with concentration. The formulas of Tollens [23] and of Nasini and Villavecchia [24] giving the values at different concentrations have been generally accepted as the most accurate. Landolt [25] combined the two, giving $[\alpha]^{20}_{5892.5\,A}=66.435+0.00870c-0.000235c^2(c=0$ to $65)$, where c is the number of grams per 100 ml of solution. This equation gives a specific rotation of 66.502° for 26.016 g per 100 ml (vacuo).

From a critical survey of the work involving the specific rotation of sucrose, performed by prominent investigators in various parts of the world, it appears that the most likely value for this constant is very close to 66.53° for 26 g of sucrose in 100 ml of solution and for sodium light (weighings in air with brass wts.).

In the light of this work Landolt's formula has been adjusted to give 66.53° at 20° C for 26.016 g per 100 ml (weighed in vacuo). The adjusted equation follows:

$$[\alpha]^{20}_{5892\,5.\,A}=66.462°+0.00870c-0.000235c^2 \tag{24}$$

This equation gives $[\alpha]=66.53°$ for 26.016 g of sucrose in 100 ml of solution and 66.54° for 16.280 g in 100 ml.

Bates and Jackson [18] in their investigation on the constants of the quartz-wedge saccharimeter made a determination of the specific rotation for two wave lengths. They found that the rotation of the normal solution for $\lambda=5892.5$ A is 34.617°, and for $\lambda=5461$ A is 40.763°. Since this solution contains 26.016 g of sugar (weighed in vacuo) in 100 ml at 20° C,

$$[\alpha]^{20}_{5892.5\,A}=\frac{100\times 34.617}{2\times 26.016}=66.529° \tag{25}$$

and

$$[\alpha]^{20}_{5461\,A}=\frac{100\times 40.763}{2\times 26.016}=78.342°. \tag{26}$$

(g) NORMAL WEIGHT OF DEXTROSE

Dextrose may be determined upon the saccharimeter, the readings being directly in percent dextrose, provided the correct normal weight for this sugar is used. This saccharimetric constant, namely the weight of dextrose, which when dissolved in 100 ml of solution and

read in a 200-mm polariscope tube with white light and bichromate filter, gives a reading of 100° S on the International Sugar Scale (conversion factor, 34.620), has been carefully determined by Jackson [26] at the National Bureau of Standards and found to be 32.231 g weighed in air with brass weights, and 32.2515 g weighed in vacuo.

For concentrations less than normal, the rotations deviate considerably from proportionality. It is therefore necessary to correct for this deviation. Table 74, page 562, gives the corrections to be applied to the scale readings in order to obtain the true percentage of dextrose. These corrections are based upon the use of a standard 200-mm tube; hence, if any other tube-length is used, this fact must be taken into account. For example, if a 400-mm tube is used, giving twice as large a scale reading as the standard 200-mm tube for the same concentration of dextrose, the observed scale reading obviously must be halved before entering the table to obtain the proper correction.

(h) ROTATION OF NORMAL SOLUTION AND THE SPECIFIC ROTATION OF DEXTROSE

Jackson found for the rotation of the normal dextrose solution the value 40.897° for the wave length $\lambda=5461$ A. The corresponding value for sucrose is 40.763° and the rotation of the normal quartz plate is 40.690°. There is thus a considerably greater difference between the rotatory dispersion curves of dextrose and quartz than between sucrose and quartz. This difference between dextrose and quartz is not as thoroughly eliminated by the bichromate filter as is the corresponding difference between sucrose and quartz (see fig. 19). A slight difference in color between the two halves of the field results when the quartz-wedge saccharimeter is set for a photometric match. This necessarily causes a lower degree of reproducibility for dextrose than for sucrose solutions. The difficulty is partially overcome by an increased number of settings or by increased experience on the part of the observer.

The specific rotation of dextrose solutions varies with the concentration according to the formula

$$[\alpha]^{20.0}_{5461\,A}=62.032+0.04257c,$$

where c is grams of anhydrous dextrose weighed in vacuo and contained in 100 ml of solution, or the formula

$$[\alpha]^{20.0}_{5461\,A}=62.032+0.04220p+0.0001897p^2,$$

where p is percentage dextrose by weight in vacuo.

(i) SPECIFIC ROTATIONS OF OTHER SUGARS

See tables 73, 75, and 76, beginning on page 562.

(j) CONVERSION AND SCALE COMPARISON FACTORS

Table 5(a) gives equivalents of various types of sugar scales in circular degrees.

Table 5(b) gives figures based upon the magnitude of the circular-degree rotations given in table 5(a) and therefore are useful only in giving an idea of the relative physical size or length of the different scales. These values cannot be used for converting from one scale into another, as the normal weight must also be taken into account.

However, they would hold as a conversion factor if, for example, 26 g were used as the normal weight on an instrument graduated on the French Sugar Scale.

TABLE 5.—*Saccharimeter scale*

[Normal weight 26.000 g, International Sugar Scale; 16.269 g, French Sugar Scale; 10.000 g, Wild Sugar Scale]

Scale	Factor	Equivalent
(a) CONVERSION FACTORS		
1° International Sugar Scale	0.34620°	Angular rotation *D*.
1° Angular rotation *D*	2.8885°	International Sugar Scale.
1° French Sugar Scale	0.21667°	Angular rotation *D*.
1° Angular rotation *D*	4.6153°	French Sugar Scale.
1° Wild Sugar Scale	0.13284°	Angular rotation *D*.
1° Angular rotation *D*	7.52814°	Wild Sugar Scale.
(b) COMPARISON FACTORS		
1° French Sugar Scale	0.62585°	International Sugar Scale.
1° International Sugar Scale	1.59782°	French Sugar Scale.
1° Wild Sugar Scale	0.38371°	International Sugar Scale.
1° International Sugar Scale	2.60614°	Wild Sugar Scale.
1° Wild Sugar Scale	0.61310°	French Sugar Scale.
1° French Sugar Scale	1.63106°	Wild Sugar Scale.

4. LIGHT SOURCES FOR SACCHARIMETERS

(a) GENERAL

It has been unfortunate in the development of saccharimetry that more consideration was not given from the beginning to the question of suitable light sources and particularly to the influence of the source on the saccharimeter reading. It has been a more or less common practice among the users of saccharimeters to employ whatever source happened to be most convenient without adequate consideration of its effect upon the reading.

The light originally used in setting the 100° point of the saccharimeter was light from the Auer or Welsbach incandescent gas mantle, filtered through a proper bichromate filter. This has been largely displaced today by the electric incandescent lamp in various forms, which is far more satisfactory from the standpoint of constancy and ease of operation. A proper filter should be used, however, in every case.

(b) BICHROMATE FILTER

While the saccharimeter is based upon the use of a quartz compensating system originally devised by Soleil, whose function is to balance out the rotation of the substance being measured by the insertion of a layer of quartz whose rotation is exactly the same in amount but opposite in direction to that of the substance being measured, yet the compensation is never absolutely complete. For white light containing all wave lengths of the visible spectrum, the compensation can be exact for only one substance, namely quartz.

Owing to the fact that the rotation dispersion curves of optically active substances are not identical, the quartz-wedge system does not completely return the polarization planes of all waves to their original

positions from which they had been rotated by the substance being tested. In the case of a solution of sugar the rotatory dispersion is nearly the same as that of quartz, but the divergence is sufficient in the green and blue end of the spectrum (see fig. 19 curves S, Q, and $S-Q$) to cause the halves of the field to appear of different tints. The field must appear uniform in color if the readings by different observers are to agree. Obviously the same instrument will also give different readings with different sources inasmuch as the luminosity curves of the sources are different. In testing sugar, the field may be made almost uniform in color for all incandescent sources of ordinary intensity by placing a cell of potassium bichromate solution between the polarizing system and the lamp. The function of this filter is to eliminate by absorption most of the shorter waves from the visible spectrum. Some saccharimeters are provided with a cell, fitted in the metal tube which houses the polarizing system, for containing the absorbing solution. Owing to their small diameter and also to the possibility of leakage inside the instrument, this Bureau has not found these cells satisfactory. Better results have been obtained by using a cell with a diameter of 40 or 50 mm placed between the saccharimeter and the light source. Any thickness may be used, but the optical path in the bichromate solution should, however, always be equivalent to a layer of liquid 15 mm thick for a 6-percent solution. If the cell is not 15 mm in thickness, the concentration of the solution must be changed accordingly. A simple rule, satisfactory for sucrose, is always to have the product of the thickness in millimeters and the percentage concentration equal to 90. In some instances where the rotation dispersion differs to a greater extent from that of quartz, as in the case of dextrose and some other sugars, it is found advisable to restrict the short-wave end of the spectrum still more by using 2 cm of a 9-percent solution, or the equivalent.

Figure 19 shows the importance of the use of a bichromate filter for white-light saccharimetry. The curve marked 6 gives the transmission (uncorrected for reflection) of a layer 1.5 cm thick of a 6-percent potassium bichromate solution, while that marked 9 gives the transmission of a 2.0-cm layer of a 9-percent solution. It will be noted that wave lengths to the left of these curves are absorbed while those to the right are transmitted. The curve marked Q shows the rotation, plotted against wave length, of the normal quartz control plate, while the curve marked S is the rotation of the normal sucrose solution. Because of the impossibility of plotting these two curves on a sufficiently large scale, they appear to be identical over most of their length, diverging slightly only in the blue, yet there are small systematic differences between them which are of great importance in saccharimetry. These differences, $S-Q$, have been plotted as a function of the wave length on a magnified scale, shown on the right, 100 times as great as that upon which S and Q separately are plotted. The dotted curve gives approximately the corresponding differences $D-Q$ between the normal dextrose solution and the normal quartz plate.

The curve $S-Q$ shows the residual amount of rotation at each wave length produced by sucrose which is not balanced out by the quartz-wedge compensating system. It will be seen that there is considerable unbalance in the blue and even in the green but that light of these wave lengths is effectively eliminated by the bichromate

solution, leaving only that part of the spectrum in which $S-Q$ is negligible in the case of sucrose. In the case of dextrose this is true to a lesser extent.

Owing to the fact that the bichromate absorption cell is indispensable when a white-light source is used and that a suitable and convenient form has not been available, the type shown in figure 20 has been designed at this Bureau especially for saccharimetric use. The cell is entirely of glass with an inner separation of the plate-glass walls of 15 mm. It is mounted in a metal frame carried on the stand, *F*. The height is adjustable with ample range to fit any saccharimeter. To utilize the filter it is only necessary to fill the cell with a 6-percent

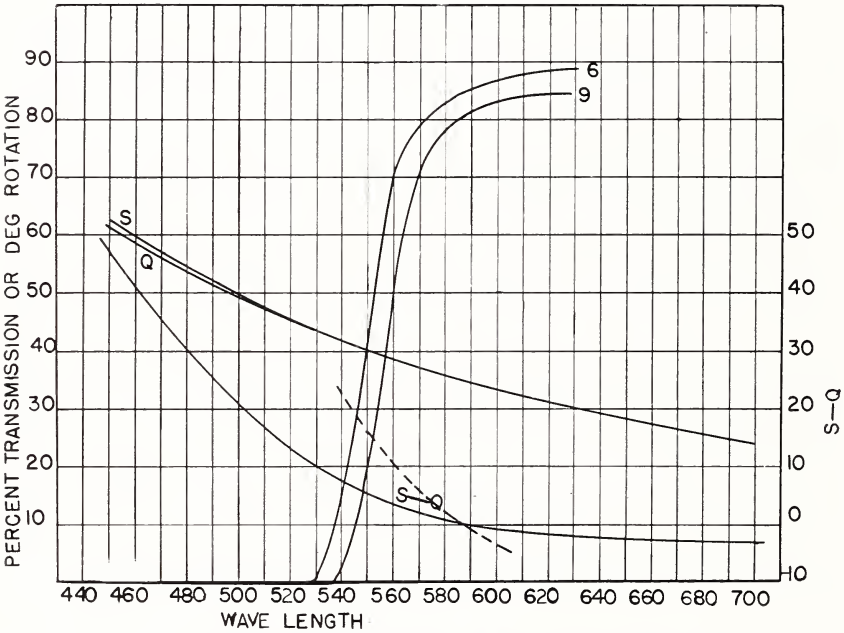

FIGURE 19.—*Spectral transmission curves for bichromate filter.*

Comparison of spectral-rotation curves for the normal quartz plate and normal sucrose solution, and the cutoff of these latter curves by the bichromate filter.

solution of potassium bichromate and place it between the light source and the polarizer, preferably as close to the latter as possible. Recently a new mount has been designed for this cell and built as an integral part of the lamp housing (fig. 21), thus doing away with the need for the separate stand shown in figure 20.

Colored glasses whose absorption very closely approximates that of the 1.5-cm layer of a 6-percent bichromate solution are now available commercially.[3] These are far more convenient to use and serve admirably to accomplish the same primary function as the bichromate solution, namely the removal of the blue end of the spectrum. However, they are open to the possible objection that they are not so efficient in removing heat rays from the lamp as is the water solution. When they are used, it may be desirable in some instances for precision

[3] Bausch & Lomb Optical Co., Rochester, N. Y.; Corning Glass Works, Corning, N. Y.

work to use a plain water cell or a heat-absorbing glass between the lamp and saccharimeter to prevent heat rays from being absorbed by the solution under test. Should colored glasses be used, care should be taken to make sure they actually have the same spectral transmission as the specified bichromate solution. Instances have been observed where saccharimeters sent to this Bureau for test were equipped with

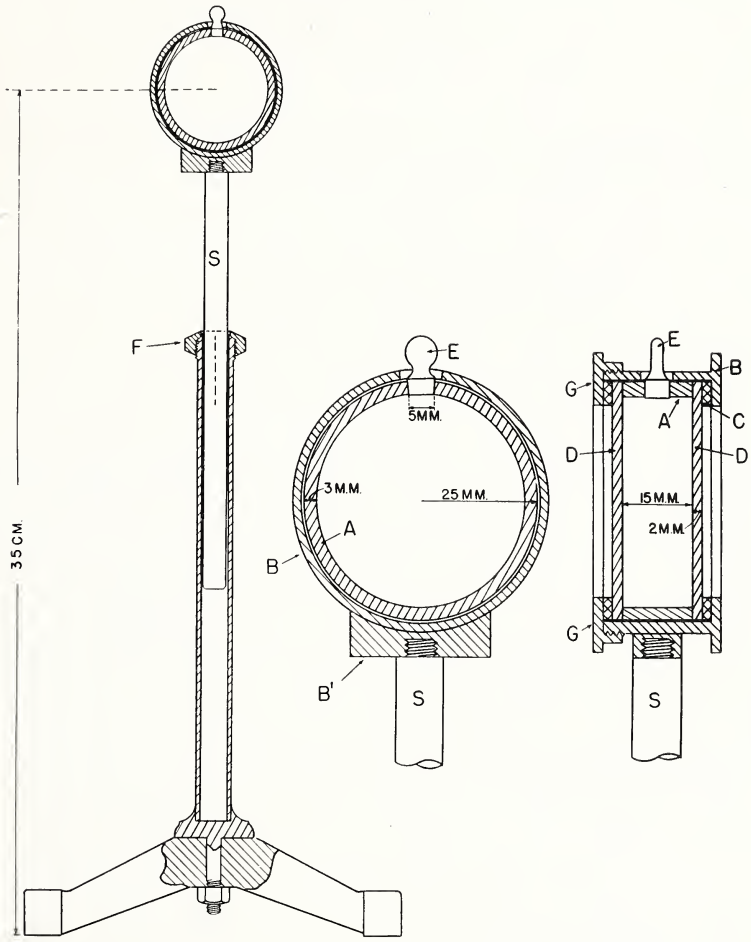

FIGURE 20.—*Bichromate filter and stand for saccharimeters (NBS design).*
A, body of glass cell; *B*, *B'*, metal cell holder; *C*, washer; *D*, glass end plates of cell; *E*, ground-glass stopper; *F*, stand and locking device; *G*, threaded cap; *S*, solid rod.

colored glasses, of foreign make, which did not even approximate the bichromate solution in their spectral characteristics.

(c) INFLUENCE ON READING

In 1904 Schönrock [16] made an investigation of the effect of different light sources on the saccharimeter reading. His results are summarized in table 6.

TABLE 6.—*Effect of light sources on the 100° S point*

Light source	Purification	Optical center of gravity	Saccharimeter reading
		λ	S^0
White light	Bichromate solution	About 6000	100.00
Sodium	Dispersion by prism	5893	100.03
Do	Bichromate solution	5893	100.03
White light	None	About 5510	100.12
"Yellow-green" mercury line	Dispersion by prism	5461	100.15
Electric	Color-glass 436^{III}	About 5200	100.224

The data in table 6 were obtained with uncolored sugar solutions. It will be observed that with a white-light source the presence of the bichromate absorbing solution makes a difference of 0.12° in the saccharimeter reading. It thus becomes important that the instrument be used under the same conditions as prevailed at the time it was standardized. If, as is usually the case, a quartz control plate is used, the plate should be read in the instrument under the same conditions as prevailed when the plate was standardized.

(d) TYPES OF LAMPS

(1) MONOCHROMATIC.—Many different types of lamps designed for use with the saccharimeter are available. They may be divided into two classes—those giving a monochromatic or nearly monochromatic light and those giving white light. In the first class only the yellow sodium lines and the yellow-green mercury line ($\lambda=5461$ Å) have been utilized to any extent and these usually for special purposes. Sources of this type must be used for circular-scale polarimeters; they are in general not satisfactory with saccharimeters which were designed for the more intense white-light source.

(2) WHITE LIGHT.

Gas.—A considerable variety of lamps suitable for white-light sources is available both for gas and for electricity. Most of the gas lamps utilize the Welsbach mantle, which is the source formerly most generally used in saccharimetry. The light is convenient, has considerable intensity, and the radiating surface has a nearly uniform intensity over a sufficiently large area. A ground-glass screen may be used close to the mantle if desired, and is necessary if the lamp cannot be so placed as to eliminate a mottled appearance of the field when the telescope is in focus for the analyzer diaphragm.

Electric.—The available electric lamps are of several types. A ground-glass disk, which becomes the new source of radiation, must, with few exceptions, be used with all types, and is preferably located as near the radiating surface as the temperature will permit. In figure 21 is shown an electric lamp developed at this Bureau, which has recently been modified to carry the bichromate filter. The concentrated-filament incandescent stereopticon lamp for 110 volts is used.[4] The area illuminated is ample for the purpose, and the intensity sufficient. Convenience has been the chief consideration in the design. The base *B* is heavy. The ground-glass disk, *R*, 38 mm in diameter, is easily removable and is adjustable vertically with respect to the body, *J*. Thus the filament and the disk may be kept

[4] The maker's identifying specifications for this bulb are G. E. Mazda, clear spotlight, 100 watts, 110 volts, C5 filament, P25 bulb, medium screw base.

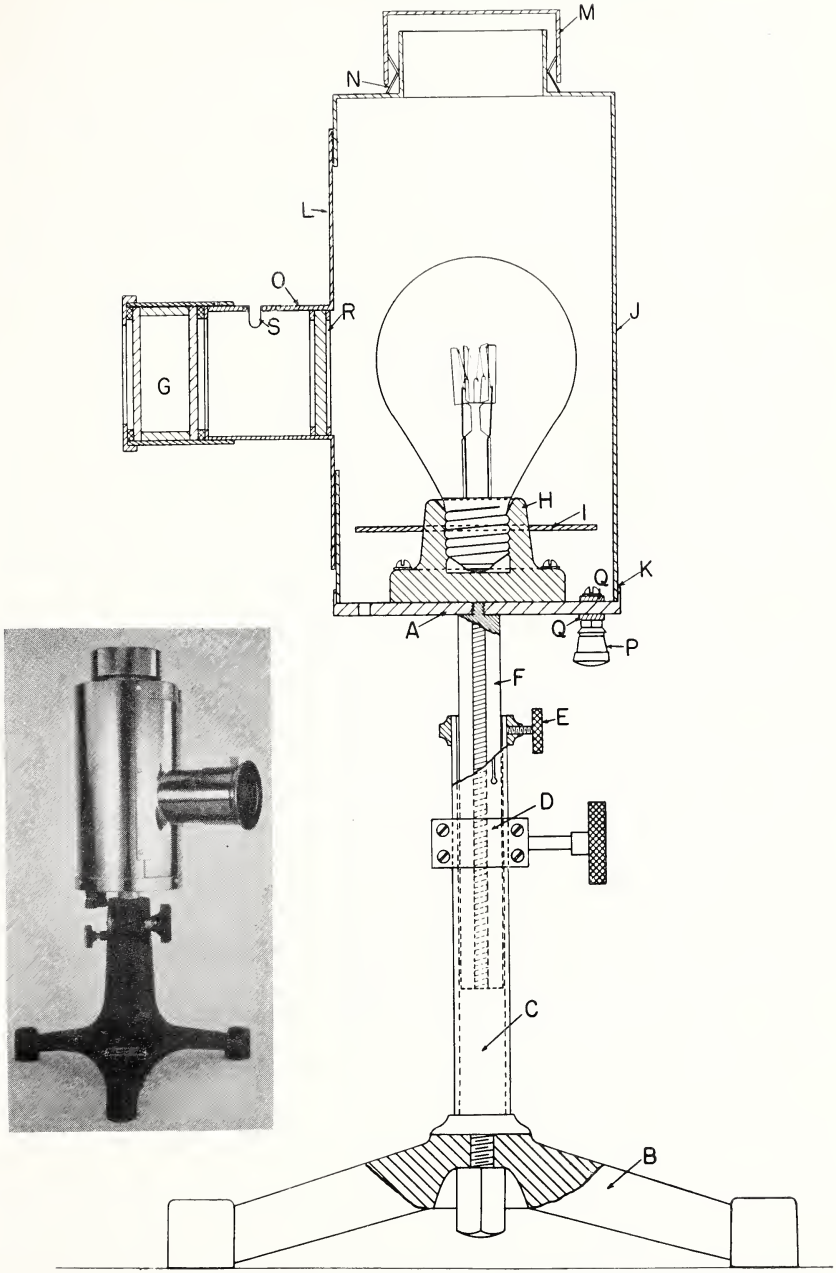

FIGURE 21.—*Saccharimeter lamp with bichromate cell holder (NBS design).*

A, base perforated for ventilation; *B*, cast-iron stand; *C*, hollow post; *D*, pinion for adjusting height of lamp; *E*, set screw; *F*, solid post fitted with rack; *G*, glass cell; *H*, porcelain lamp socket; *I*, removable disk light screen; *J*, lamp housing fitting into flange, *K*; *L*, adjustable slide; *M*, removable cover held by springs, *N*; *O*, side tube carrying ground glass and bichromate cell; *P*, binding posts; *Q*, insulating blocks; *R*, flange to hold ground-glass plate; *S*, slot opening for ventilation.

centered, giving uniform illumination of the disk. The cap, *M*. permits the heat to pass off but no light to escape into the room, The height of the lamp is regulated by the rack and pinion, *D*. The center of the disk can thus be accurately set in the axis of the optical system of the saccharimeter. The electric connection is made at the binding posts, *P*. This lamp has proved very satisfactory in the laboratories both of this Bureau and of the United States Customs Service and is the type most highly recommended for general use. The firm of Schmidt & Haensch has taken advantage of the small size of the 6-volt lamp to mount it in an attachment which fits the metal housing containing the polarizing system of their saccharimeter.

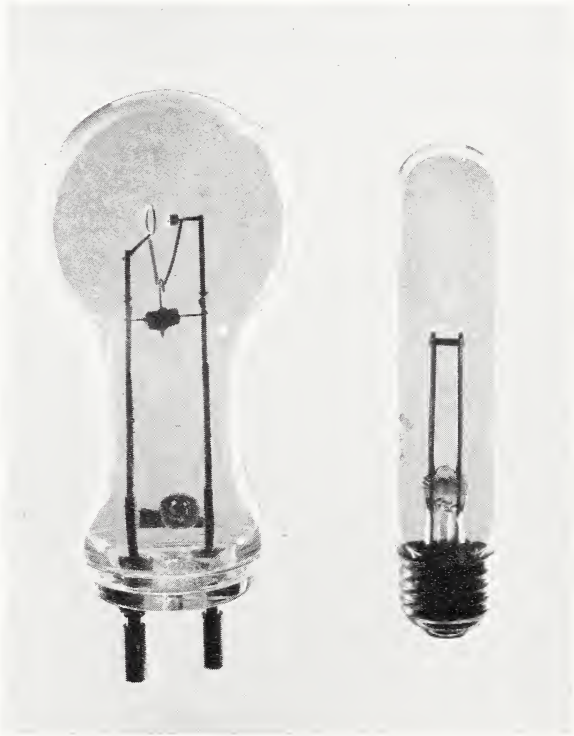

FIGURE 22.—*White-light sources.*
Left, tungsten arc in vacuum (30-ampere arc); right, ribbon-filament lamp (6 volts, 108 watts).

The heat developed so near the optical parts is objectionable. The illumination is only fairly satisfactory when the lamp is new, and the efficiency in most cases decreases rapidly with use.

In special cases where the 100-watt lamp does not yield sufficient light, other sources have been utilized.

The Nernst glower was useful for some years but is now of little more than historical interest. It has been largely displaced by incandescent stereopticon bulbs of higher wattage than that described above. They are obtainable in 250-, 500-, and 1,000-watt ratings.

Other high-intensity sources are (1) (fig. 22 right) the 6-volt, 108-watt ribbon filament lamp, which is operated from a small transformer; and (2) (fig. 22 left) the tungsten arc in vacuo developed by

the General Electric Co. as a source for photomicrographic work. The latter is a 30-ampere arc in a small glass bulb, the incandescent tungsten electrode serving as the light source. It is operated by a special high-reactance transformer operating from the 110-volt alternating-current line. Both of these types can, by the use of proper optical systems, be made to give uniform polariscopic fields without the use of the ground glass, thereby greatly increasing the intensity available. Such sources, however, find only limited uses and for very special purposes. The 100-watt lamp described above in detail is adequate for all ordinary work.

5. CERTIFICATION OF QUARTZ CONTROL PLATES

Quartz control plates for use in checking saccharimeters will be accepted by this Bureau for standardization with reference to the sugar value. The conditions as to mounting, purity of quartz, correctness of fabrication, etc., are given on page 57. This Bureau reserves the right to reject any plate showing defects which may render it unreliable or otherwise unsatisfactory in service.

Certificates are issued showing the optical rotation of the plate for pure monochromatic light of two wave lengths, $\lambda = 5461$ A and 5892.5 A, as well as the sugar value of the plate at 20° C in International Sugar Degrees. When desired, an accompanying table of temperature corrections will be furnished covering the range 15° to 30° C, by means of which saccharimeter readings made at any temperature within that range may be corrected to the reading that would have been obtained had the readings been made at 20° C.

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V. TEMPERATURE CORRECTIONS AND CONTROL

1. QUARTZ-WEDGE SACCHARIMETER

The question of temperature corrections for polarimetric apparatus, as well as for the optically active substances, is a difficult one. The literature on this subject is extensive, but it has not always been a simple matter to select the proper correction owing to the different results secured by various investigators. For the ordinary polarimeter used for measuring absolute rotations no instrument correction is necessary. It may be used at any temperature if care is taken to allow for any zero-point shift that may occur. However, a correction is unavoidable for saccharimeters, in which a quartz wedge is used to neutralize the rotation of the substance being tested if temperatures other than the standard are used. The rotation for a plate of quartz in the neighborhood of 20° C is given by the following:

$$\alpha_t^D = \alpha_{20}^D + \alpha_{20}^D \, 0.000143(t-20). \tag{27}$$

The linear coefficient of expansion of quartz perpendicular to the optic axis is 0.000013, and of the scale is 0.000018 if it is of nickelin, and 0.000008 if it is of glass. Thus the total temperature coefficient [1] for the ordinary quartz-wedge saccharimeter is

$$0.000143 - 0.000013 + 0.000018 = 0.000148 \text{ (metal scale)} \tag{28a}$$

or

$$0.000143 - 0.000013 + 0.000008 = 0.000138 \text{ (glass scale)}. \tag{28b}$$

If the scales were etched on the wedges, the scale coefficient would become zero. Since the effect of the expansion coefficient 0.000148 is to lower the reading of the scale with an increase of temperature, the apparent polarization of any substance is lower than it should be and the reading at 20° (S_{20}) is given by the following:

$$S_{20} = S_t + S_t \, 0.000148(t-20). \tag{29}$$

When a quartz control plate is read in a saccharimeter, this effect is not completely compensated. Since the temperature coefficient of the plate is 0.000143, the reading (S_{20}) of the plate is then

$$S_{20} = S_t + S_t \, 0.000005(t-20). \tag{30}$$

The correction given by this equation changes sign if the scale is of glass, and is so small at all times as to be negligible in ordinary polarizations.

2. SUCROSE

The influence of temperature on the specific rotation of sucrose has been studied by numerous investigators, of whom Dubrunfaut [2] was the first to discover that the constant decreased with increase in temperature. Unfortunately, subsequent determinations of this variation have not shown satisfactory agreement.

Schönrock [3] at the Reichsanstalt carried out an elaborate investigation and found that for the normal sugar solution (p=23.701) the temperature coefficient (δ) was independent of the wave length of the light used, but that it decreased with increase in temperature as follows:

10° C, 0.000242; 20° C, 0.000184; 30° C, 0.000121.

These data show the change to be practically linear over the range 10° to 30° C, and have been combined into the following equation [4, p. 7]:

$$\delta = -0.000184 + 0.0000063(t - 20° \text{ C}) \tag{31}$$

3. COMBINATION OF CORRECTIONS FOR QUARTZ-WEDGE SACCHARIMETER AND SUGARS

If a proper temperature correction is to be applied to a polarization, it is necessary to add algebraically all the corrections applicable to the conditions under which the polarization is being made, or to determine the correction experimentally.

(a) SUCROSE

In the ordinary testing of sucrose, the solution is made up to volume and read at the same temperature, which in general is not the standardization temperature. It is desirable, therefore, to know the variation with temperature in the saccharimeter reading of a near normal sucrose solution.

Among the factors that require consideration are the changes in the quartz-wedge system due to changes in temperature, changes in the specific rotation of sucrose, in the volume of solution, in the volume of the flask, and in the length of the tube used. Some of these act in opposite directions and thus partially cancel or compensate for each other.

By a summation of the best known values of the separate coefficients which enter into the correction factor, we obtain the value 0.0309 per degree centigrade for a normal sucrose solution (100° S).

Owing to its importance, this over-all temperature coefficient has been measured experimentally by a number of investigators. Their results are given in table 7, based upon a normal solution of sucrose.

TABLE 7.—*Saccharimeter temperature coefficient for sucrose*

Investigator	Temperature coefficient	Investigator	Temperature coefficient
Andrews	0.0300	Watts and Tempany	0.0310
U. S. Coast and Geodetic Survey	.0293		
Wiley	.0314	Average	0.0303
Geerligs	.0300		

The average value obtained is 0.0303 for a normal sugar solution (100° S). The value varies slightly for different instruments, probably in part because of slightly different differential expansions of the scale and wedge mountings.

This correction factor is predicated upon the instrument and all apparatus, flasks, tubes, etc., having been originally calibrated at 20° C but used at some other temperature between 20° and 30° C. It is important and necessary, for the proper application of this temperature correction, that the solution be made up to volume at the same temperature as that at which it is to be read in the saccharimeter and that the entire saccharimeter also be at that same temperature.

323414°—42——8

Under these conditions the polarization in sugar degrees at 20° C (S_{20}) of an approximately normal sucrose solution made up to volume and polarized at the same temperature (t° C) is given by the following:

$$S_{20}=S_t+S_t\ 0.0003\ (t-20°\ \mathrm{C}). \tag{32}$$

This equation is sufficiently accurate for all ordinary polarizations, irrespective of type of tube or scale.

(b) APPLICATION OF TEMPERATURE CORRECTION BY MEANS OF A QUARTZ CONTROL PLATE

This correction is most conveniently and satisfactorily applied by means of a standardized quartz control plate. The proper use of such a plate gives an over-all correction which includes not only the above temperature correction but also corrects any accidental or irregular variations, such as those due to minor residual temperature differences in the quartz wedges, etc.

The procedure in using a quartz control plate is quite simple and is as follows:

When making a series of polarizations of sugar solutions on the saccharimeter, also make a series of readings on the standard quartz control plate. Observe the temperature. From the table of sugar values for the standard plate find the sugar value corresponding to the observed temperature. The difference between the observed reading of the plate and the sugar value obtained from the table is applied as a temperature correction to all polarizations made during that series.

This is the procedure which has long been recommended by this Bureau whenever making polarizations where a standard 20° C constant-temperature room is not available.

Because of its convenience and accuracy this practice was introduced by the Bureau into the various Customs laboratories at a very early date. Figure 23 is a facsimile copy of a table showing the sugar values for various temperatures of a quartz control plate, which was issued in 1907 as a part of the certificate of test for that plate. Prior to that date similar tables were issued and are still being issued whenever requested in connection with the certificates for quartz control plates. (See this Circular, p. 553, Fee Schedule 423e; Circular C44, Polarimetry, 2d edition (1918), p. 111, Fee Schedule 44d; Circular C44, 1st edition (1914), p. 96, Fee Schedule 44d).

These tables are based upon the measured value of the plate at 20° C and the saccharimeter temperature coefficient 0.0003, as defined above. They are calculated from the equation

$$S_t=S_{20}\ [1+0.0003\ (t-20°\ \mathrm{C})] \tag{33}$$

and are valid, of course, only under the conditions stated above, namely, that the solution be made up and polarized at the same temperature.

(c) CORRECTIONS FOR USE IN TROPICAL COUNTRIES

Temperature correction by the method outlined above is frequently utilized and gives excellent results in tropical countries, and it is

Department of Commerce and Labor

Bureau of Standards

Certificate

FOR

Quartz Polariscope Control Plate

Maker: Schmidt and Haensch B. S. No. 226-BS-1907

SUBMITTED BY

Treasury Department
Washington, D. C.

Degrees Centigrade	Sugar Value	Degrees Centigrade	Sugar Value	Degrees Centigrade	Sugar Value	Degrees Centigrade	Sugar Value
13°0	99°77	20°0	99°98	25°0	100°13	30°0	100°28
14°0	°80	20°5	100°00	25°5	°15	30°5	°30
15°0	°83	21°0	100°01	26°0	°16	31°0	°31
16°0	°86	21°5	°03	26°5	°18	31°5	°33
17°0	°89	22°0	°04	27°0	°19	32°0	°34
17°5	°91	22°5	°06	27°5	°21	32°5	°36
18°0	°92	23°0	°07	28°0	°22	33°0	°37
18°5	°94	23°5	°09	28°5	°24	34°0	°40
19°0	°95	24°0	°10	29°0	°25	35°0	°43
19°5	°97	24°5	°12	29°5	°27	36°0	°46

E. B. Rosa
Acting Director.

F. J. Bates
In charge of test.

Test No. 2633
Dec. 16, 1907

Washington, D. C.

11—1784

FIGURE 23.—*Facsimile of certificate for quartz control plate 226–BS–1907.*

preferable to adopting a different standardization temperature, such as 25° or 27.5° C, as sometimes suggested.

Einsporn and Schönrock [4] have made an elaborate study to find by calculation what the corrections would be if the polarization is carried out at the tropical temperatures of 25° and 30° C. Their final values are identical with those which this Bureau has always given for these temperatures in its tables of temperature corrections accompanying quartz control-plate certificates. (See fig. 23.)

If the solution is made up to volume at 20° C, but is polarized at another temperature, all apparatus being at that temperature, equation 32 is no longer applicable. Under these conditions the temperature coefficient of the normal sucrose solution alone is given by Schönrock as 0.000469, while that of the saccharimeter, as previously shown, is 0.000148. If a glass tube is used, we have as the total temperature correction

$$0.000469-0.000008+0.000148=0.000609.$$

The polarization in sugar degrees at 20° C (S_{20}) of the near normal solution of sucrose is therefore given by

$$S_{20}=S_t+S_t 0.000609\ (t-20°\ \mathrm{C}). \tag{34}$$

Equation 34 obviously holds only while the number of grams of sugar in 100 ml of the solution remains unchanged.

(d) SUGAR MIXTURES

The coefficient 0.0003, in eq. 32, having been determined for the normal weight of sucrose, should be applied with considerable care. It has, however, long been a widespread practice to apply it to all sorts of saccharine products, with the result that a polarization, supposedly accurate, may contain errors of appreciable magnitude. If the solution does not read approximately 100° S, the correction to give the reading at 20° C should not be obtained by multiplying 0.03 by the difference in temperature—a common practice. In general, no great error will be introduced by following this procedure provided the polarization is above 85° S. Nevertheless, the better and safer practice is to solve eq 32, thereby correcting for the difference in sucrose concentration from the normal solution.

An even more widespread practice has been to apply eq 32 to sugar polarizations without regard to the associated impurities. This is particularly true of raw sugars and molasses which contain appreciable quantities of invert sugar. Of the constituents of invert sugar, the dextrose has a negligible temperature coefficient, while the levulose has a very large coefficient, and in such a direction that the positive rotation of the mixture tends to increase upon elevation of temperature.

It is therefore manifestly erroneous to apply a pure sucrose temperature coefficient to a mixture unless all the substances, except sucrose, are present only in such small quantities that the error introduced is negligible.

For the temperature correction of the better grades of raw sugar, the temperature formulas 32 and 34 give results which are sufficiently accurate; but if they are applied to low-grade products, errors are

introduced. Raw sugars may be considered as mixtures of pure sucrose and cane molasses. To correct the whole mixture for the effect of temperature change, it would be necessary to apply the resultant coefficient obtained by combining the separate coefficients for sucrose and for molasses, taking into consideration the relative quantities of the two and the constitution of the particular molasses which contaminates the sample. C. A. Browne [5] has done this and shows that the temperature coefficient varies in almost direct proportion to the content of molasses. It is in general incorrect to apply this computed correction because of possible individual variation in the constitution of the molasses. Accordingly Browne advises the omission of the temperature correction for low-grade samples. He has computed an average coefficient for large numbers of samples of raw sugar which may be determined according to the polarization. Thus for cane products the coefficient is 0.0015. It is seen from this that at 80° the coefficient becomes zero and for lower grades it becomes positive instead of negative. If individual variations did not occur, this correction would be a useful one; but as it stands, it merely serves to show the possible error of applying eq 32 to low-grade sugar. For beet products the coefficient is 0.0006.

4. THERMOSTATS

(a) WATER

The satisfactory control of temperature in polarimetric work is an important and troublesome subject. For accurately making up solutions to volume at a desired temperature, water thermostats which give extremely close regulation are to be preferred. Many types which are entirely satisfactory are available from apparatus dealers. These consist essentially of metal or glass tanks suitably insulated on the outside and nearly filled with water. The cooling is accomplished by circulating ice water through an immersed coil, and the temperature regulation is maintained by immersed lamps or heaters operated intermittently by means of mercury relays connected to mercury thermoregulators. The water is kept in constant motion, insuring an even temperature throughout, by means of electric turbines or stirrers. For circulating constant-temperature water through the jackets of polariscope tubes, refractometers, etc., use is made of small electric-driven pumps.

(b) AIR

At the National Bureau of Standards most polariscopic measurements are made in a constant-temperature room maintained at the standard temperature of 20° C. Three such rooms are available. The largest of the three, used for both routine and research work, is approximately 10 by 20 feet. The walls and ceiling are insulated with thick corkboard. The temperature is maintained by the automatic intermittent operation of a large ammonia compressor located in the attic room above, the direct-expansion ammonia coils being mounted on the side walls of the constant-temperature room. Satisfactory temperature control is accomplished through the use of a bimetallic regulator.

The saccharimeters are placed within the room on a table of convenient height. For special work the instruments are enclosed in

individual insulated boxes. This so retards any change in temperature of the instrument that, when the room is operating within a few tenths of a degree, no significant change can be detected on the thermometer inside the instrument case after equilibrium is reached. The illumination of the instrument is secured by placing suitable light sources just outside the room, allowing the light to pass into the room through small glass windows in the walls.

One of the rooms used for special research work, in which the Bureau's large polariscope, described on page 46, is located, is approximately 7 by 10 by 9 ft. with an adjoining closet in which is housed refrigeration coils feeding from the central refrigerating system (CO_2) of the Bureau and controlled by a needle valve on the intake side (fig. 24). A fan, *F*, located in an opening near the top of the closet blows cold air from around the refrigeration coils, RC, out into the room into the space above a false ceiling, *C*, which is perforated throughout and serves to distribute the cold air evenly over the top of the room. An opening near the bottom of the closet allows return air to be sucked into the closet to be recooled. Cold air is prevented from circulating in reverse direction, when the fan is not operating, by means of a valve, *V*, consisting of a flap of heavy cloth tacked across the upper edge of the bottom opening. When the fan stops, the cloth falls against the opening and effectively seals it against the cold air in the closet.

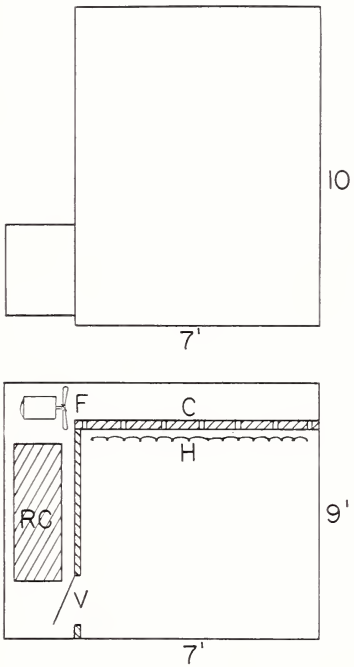

FIGURE 24.—*Constant-temperature room.*

Upper, basal section; lower, vertical section.

Thus cold air is fed into the room only while the fan is operating and in an amount depending upon the speed of the fan.

A heater, *H*, attached to the lower side of the false ceiling may be operated when needed, either continuously by a switch or automatically by a thermostat. This heater is used, however, only when temperatures above outside room temperature are required.

The fan which controls the amount of cold air put into the room is operated automatically by a bimetallic-strip regulator through an electronic relay. This avoids the use of all mechanical relays and their troublesomeness.

The assembly used for operating the fan is shown in figure 25 and is largely self-explanatory.

It is essentially a full-wave grid-controlled rectifier arranged for on and off or relay operation. It was assembled from stock parts which were immediately available, with a view to extreme flexibility and adaptability to other uses. Had it been engineered only for the par-

ticular job in hand, considerable simplification could have been made. For instance, the variac, T_1, could have been dispensed with and also a much smaller transformer of the correct voltage and power rating used in place of T_2. However, the apparatus as assembled has proved very convenient and dependable in operation and has a power-handling ability of over 500 watts.

In operation, current is first switched onto the filament lighting transformer, T_3, and the filaments of the FG 57's allowed a heating time of about 5 minutes before switching on the plate power, T_2. For the sake of simplicity of the drawing, the filaments are shown lighted by separate transformers. In practice they may just as well be paralleled on a single 5-volt winding.

After the filaments have reached their operating temperature, the switch, S, is closed, activating the variac, T_1, whose output tap

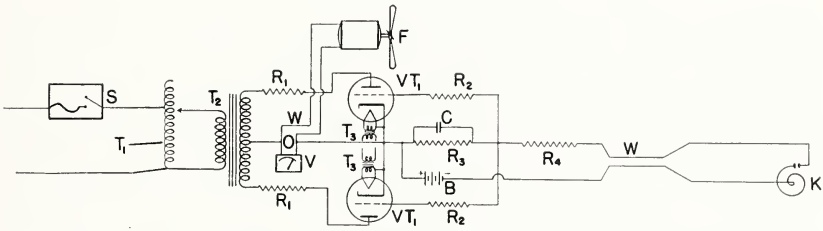

FIGURE 25.—*Wiring diagram for electronic-relay control of thermostated cold room.*

T_1, GR Variac, 200 CM; output voltage, 0 to 130 volts; T_2, GE transformer No. 9TM416A; primary 683 kilovolt amperes, secondary 990 kilovolt amperes, 110/220/55 to 550/275 volts; T_3, Filament transformer, 110 to 5 volts, 50 watts; S, Fuse and switch; VT, Thyratrons FG 57; plate current, 2.5 amperes each, maximum average; 1,000 volts, maximum peak; filament, 5 volts, 4.5 amperes each; R_1, 20-ohm resistors (660-watt heater units with medium screw base) mounted in porcelain lamp-socket bases; R_2, 50,000-ohm, 1-watt resistors; R_3, 100,000-ohm, 1-watt resistor; R_4, 10,000-ohm, 1-watt resistor; C, 1-microfarad capacitor; B, 7.5-volt bias battery; K, American Instrument Co. "Quickset" bimetallic regulator; V, Direct-current voltmeter, for use when adjusting the load voltage by means of T_1; O, Hubbell plug which serves as output terminals; F, Fan located in cold closet; and W, Twisted lamp-cord leads.

has been set at or below the proper operating position for the particular load, which is connected through a Hubbell plug at O. When first adjusting the apparatus, the voltage on the primary of T_2 is varied by means of the variac, T_1, until the direct-current voltmeter, V, shows the correct voltage across the load at O, which in this case is the fan motor, F. Thereafter the variac may be left at its proper setting and the power simply switched on at S.

For the particular fan at present in use, about 70 volts is required on the input side of T_2 to maintain the fan's rated voltage of 120 volts at O.

The resistors, R_1, are ballast resistors to protect against current surges and extreme overload on the tubes made possible by the non-resistive character of the load (fan motor). Even if the load were short-circuited, R_1 would limit the current to the point where the tubes and transformer would not be injured before the fuse could blow or an overload relay, if used, could operate. Heater units, 110-volt 660-watt, such as are used in the ordinary household electric reflecting heater, serve admirably. They consist of resistance wire wound on a ceramic cone which carries a screw plug on one end similar to that on ordinary incandescent lamps and which fits the ordinary medium screw-base lamp socket.

Load current is not passed by the tubes as long as the grids are kept sufficiently negative. When the contacts of the bimetallic regulator, K, are open the grids assume practically ground or cathode potential and load current normally flows, operating the fan. When sufficient cold air has been blown into the room to cause the contact, K, to close, the battery, B, operating through the networks $R_2R_3R_4$, impresses a negative bias on the grids sufficient to block off the plate current and stop the fan. Since this battery, which is an ordinary 7½-volt radio C battery, is only connected in the circuit intermittently,

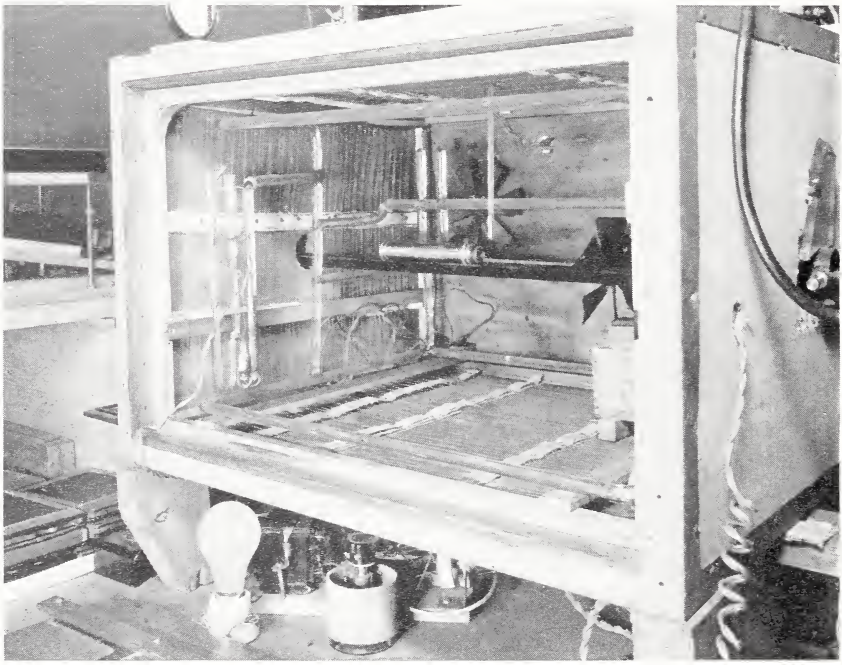

FIGURE 26.—*Inside view of polariscope air bath (thermostated).*

and then through a high resistance of more than 100,000 ohms, its expected life is not much less than its shelf life.

The condenser, C, serves to stabilize the grid-cathode difference of potential and at the same time, in connection with R_4 and R_3, serves as a time-delay device, to delay starting or stopping until after K makes good contact or breaks contact. This aids in eliminating chattering due to mechanical vibrations when the contacts, K, are nearly closed. R_3 serves to discharge C after K opens, thus allowing the grid to return to cathode potential and start the fan. R_4 serves to limit the rush of charging current to C when K closes, preventing sparking at the contact, K. By use of this device the temperature of the room may be maintained constant at any desired temperature within the range of the cooling system, for long periods of time, with a variation of only a few tenths of a degree. The exterior walls of the room are cork-insulated. Provision also is made for cooling the room in wintertime by the use of outside air instead of refrigeration, by blowing the cold

outside air through a duct into the room. The fan for this also may be plugged in at *O* and operated thermostatically either instead of or in parallel with the fan in the cold closet. Lamp-cord connections are used at *W* and permit the relay to be located at any convenient place, since their length is immaterial.

The air bath (fig. 26) on the polariscope mentioned on page 46 is located in this room. In operation the room temperature is set at from one-half to 1½ degrees below that desired in the polariscope thermostat. The temperature of the latter is then brought up to and maintained at the desired temperature, usually 20° C, by an electric heater whose windings are fairly uniformly distributed around four surfaces of the box, as indicated in the photograph. A slight increase

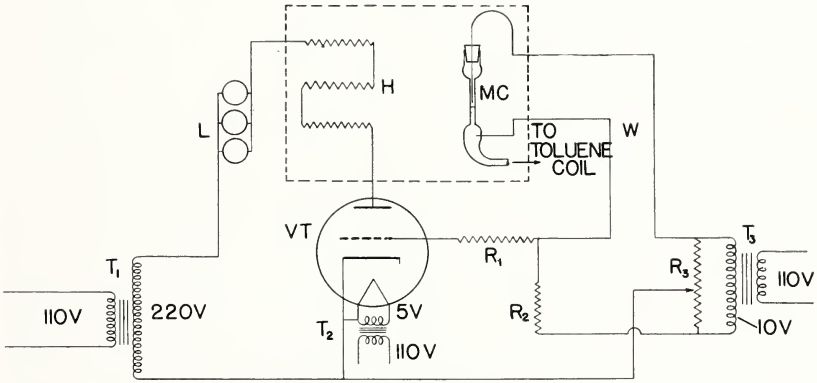

FIGURE 27.—*Wiring diagram for electronic relay control of polariscope air bath (fig. 26).*

T_1, 110- to 220-volt transformer, about 100 watts; T_2, Filament-lighting transformer, 110 to 5 volts, 4.5 amperes; T_3, Biasing transformer, 110 to 10 volts, 0.1 ampere. Note that T_2 and T_3 may conveniently be separate windings on T_1; *VT*, Thyratron *FG* 57; R_1, 50,000-ohm, 1-watt grid resistor; R_2, 1-megohm, 1-watt resistor; R_3, 200-ohm potentiometer (not needed if T_3 is supplied with a mid-tap); *L*, Lamp sockets for the insertion of different-wattage lamps as series resistance for *H*; *H*, Heater-winding in thermostat; *MC*, Mercury-platinum contact contained in 1-mm capillary tube connected to toluene coil; and *W*, No. 20 lamp-cord leads to mercury contact.

in temperature causes toluene in the glass tubing, fig. 26, to expand and close the mercury contact, *MC*, figure 27. This figure shows the wiring diagram for the relay and heater. The transformer, T_3, working through the resistors $R_1R_2R_3$, when *MC* is closed, impresses a negative bias on the grid of the Thyratron, *VT*, sufficient to block off the plate current. When *MC* opens, this negative bias is removed and plate current again passes, since the grid potential then becomes 0 or positive, according to the position of the tap on R_3. If a 10-volt middle-tapped transformer is available, R_3 is not necessary.

The heater, *H*, and the mercury contact may be seen in the photograph. The lamps, *L*, are outside the thermostat and serve to control the current in *H* without the necessity of varying the input voltage to T_1. Ordinarily a single 50-watt lamp gives about the right amount of series resistance, since only a few watts are required in *H* when the surrounding temperature is only about 1° below that of the thermostat. The air in the thermostat is stirred by means of a fan driven by a small electric motor. The temperature remains constant to 0.01° C or

better. No variation can be seen on a 0.1° thermometer read by a telescope, where 0.01° C would readily be detected. There are no moving contacts to give trouble, and this relay has been left in operation for months at a time with no attention whatever. The current made and broken at the Hg-Pt contact, *MC*, has been reduced to a very small value, which largely eliminates contamination of the mercury due to arcing or sparking. If a screen-grid Thyratron, such as the FG 95, is used in place of the FG 57, the resistance in series with the contacts, *MC*, may be increased to several megohms without loss of reliability, still further reducing the current in *MC*.

Recently a third constant-temperature room has been installed, designed to permit polariscopic measurement over a wide range of temperatures. The room is insulated by a 6-inch layer of cork on all walls, ceiling, and floor; the inner surface is finished in cement plaster on the walls, and thick cement floor. In the attic above is located a large insulated brine tank, cooled by immersed coils connected to the central system of liquid CO_2 refrigeration. The cold brine is circulated through cooling coils mounted in the constant-temperature room by means of an electrically driven pump. The circulating pump may be run intermittently by a thermostat or continuously as desired. The cooling coil in the room is mounted in a so-called cooler placed near the ceiling. A large fan located in the cooler forces air over the coils and distributes it through a duct running the length of the room. The duct is fitted with suitable adjustable openings, permitting even distribution of the cooled air. A thermoregulator controls the pump which circulates the brine through the coolers. Other thermostats control heaters mounted within the duct. Constant temperatures may be maintained within the room over a temperature range of from −30° to +30° C.

5. REFERENCES

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VI. ACCESSORY APPARATUS

1. POLARISCOPE TUBES*

(a) TYPES

(1) Ordinary.—There are available at present a variety of polariscope tubes each designed to give satisfactory results under certain conditions. In making a selection, the user must be guided by his own particular needs. In general, polariscope tubes should be constructed to meet three essential requirements, and if these are not met by the device as furnished by the maker, the faults cannot be remedied by the user. These requirements are (1) parallel ends which are perpendicular to the axis of the tube, (2) accurate length, and (3) accurate centering of the axis of the tube in the trough of the saccharimeter. In most instruments the center of the optical path is approximately 15 mm above the bottom of the trough. The type for ordinary

*See test-fee schedule 297, p. 555.

polarizations at temperatures not far removed from 20°C is the simplest, but, unfortunately, has received least consideration. Its design should have careful study, even to the slightest detail. This is essential owing to its widespread and constant use for both scientific and commercial purposes.

An all-metal tube of small bore (fig. 28, No. 4), being one type that is in more or less general use, has the same diameter for the entire length. These tubes frequently are constructed with walls so thin that they are easily bent or distorted, resulting in a change of length and ruining the tube. In many cases the bore is too small. The diaphragming in the modern saccharimeter is designed to give the highest possible illumination of the field. To utilize this as well as to eliminate the undesirable "halo" in the field of the instrument, it is necessary that the bore have a diameter of not less than 9 mm. Considerable time is lost in filling owing to the fact that the tube must be so completely filled that no air bubble remains. The weight of the tube is carried upon the caps which hold the cover glasses. If the tube is rotated in the trough of the instrument, the caps may be tightened, and the additional pressure may cause double refraction in the cover glasses, which has the effect of changing the rotation of the plane of polarization.

Glass tubes must be used when the solutions contain acid or other corrosive chemicals. Metal collars threaded to fit the screw caps are cemented on. Wax is sometimes used for this cementing, but this is objectionable on the ground that the wax sometimes softens and permits the collar to be displaced until it extends over the end of the tube. Thus the length of the column of liquid being polarized is increased and an error introduced in the observation. A mixture of glycerine and litharge or a similar cement is more satisfactory, and the ends of the glass tube should not extend more than 1 mm beyond the threaded collar.

(2) Bates.—In the laboratories of the U. S. Customs Service, as well as in other laboratories, there is required a tube which is both rugged and as free as possible of defects. The Bates tube (fig. 28, No. 1) designed at this Bureau, has proved to be entirely satisfactory in meeting these requirements. It will be observed that the weight is carried upon two shoulders, which are integral parts of the tube, and not upon the caps, thereby eliminating all danger of tightening when the tube is rotated in the trough of the instrument. The bore is 9 mm, permitting the utilization of the full aperture of the polarizing system. This also reduces to a minimum the light depolarized by reflection from the walls of the tube. The field of the instrument appears as a bright circle with no overlying haziness, and permits readings of increased accuracy. Both ends are enlarged with all the attendant advantages; hence but one size cover glass and washer is required. The walls are unusually heavy, eliminating all danger of bending. These tubes are available in 400-, 200-, and 100-mm lengths. Glass tubes of the same design are also in general use.

(3) Special.—There are a number of tubes available for special purposes. For polarizations, where the temperature must be controlled or measured, a water-jacketed tube is recommended (fig. 28, No. 2). This consists of an inner tube of either metal or glass having a tubulature midway between the ends to permit filling and inserting a thermometer. A watertight jacket of metal surrounds

the inner tube provided with a nipple at each end to allow the circulation of hot or cold water. Landolt has designed a glass tube with one end enlarged and having sliding caps which fit over metal mounts, this construction being intended to eliminate the possibility of excessive pressure on the cover glasses. This tube has been modified by having the caps held in place by bayonet catches. However, the Landolt tube has not been generally used in the United States. Tubes provided with screw caps are preferred by most chemists, and if care is taken not to tighten the caps too much, they are entirely satisfactory.

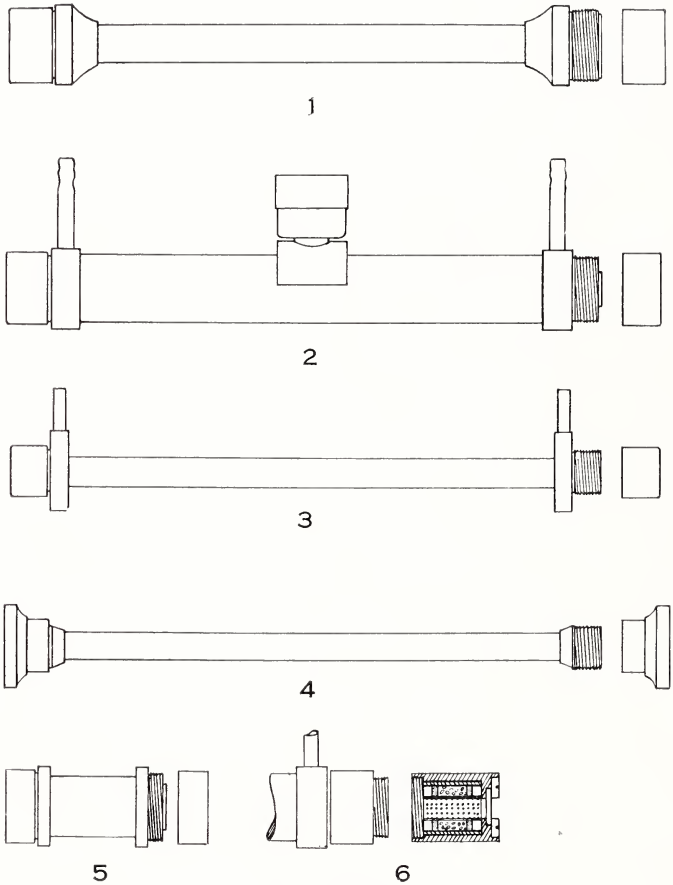

FIGURE 28.—*Polariscope tubes.*

The continuous-flow tube of Pellet (fig. 28, No. 3) is widely used in factory control work. It is provided with a tubulature at each end, permitting filling and emptying without removing the tube from the instrument. The tube is filled by pouring the solution through a small funnel into one of the tubulatures. After the polarization, the succeeding solution is poured into the tube, displacing the first solution. These tubes effect a saving of time and are satisfactory for use with solutions of approximately the same polarization. Yoder devised a volumetric tube having the graduation mark on the connec-

tion joined on the middle of the tube. The usual size is 10 ml, but tubes of various volumes may be constructed by varying the length and bore.

When the temperature of the solution is below the dew point, moisture condenses on the cover glasses. Wiley has overcome this by an ingenious desiccating cap (fig. 28, No. 6), which carries calcium chloride or other desiccant, and screws to the end of the polariscope tube.

A special glass-lined Bates tube is shown in figure 28, No. 5. It is made in 50- and 25-mm lengths and is useful in cases where a limited volume of liquid is available or where high rotating liquids are to be measured.

(4) Water-Jacketed for High-Temperature Polarization.—It is frequently necessary to make polariscopic observations at high temperatures. Difficulty has been experienced in such measurements, using the ordinary water-jacketed tubes, due to leakage and distortion of the field caused by uneven heating. There has recently been developed at this Bureau a tube designed to eliminate the existing defects. The new tube, figure 29, is constructed entirely of an iron-nickel alloy having practically zero expansion for temperatures from

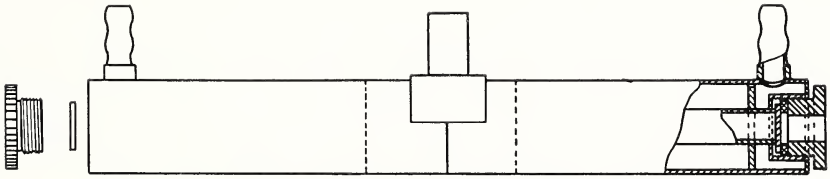

Figure 29.—*High-temperature polariscope tube (NBS type).*

0° to 100° C. The tube is welded into a water jacket which extends well beyond the end of the inner tube, thus maintaining an even temperature throughout the length of the liquid-column under observation. The tube is provided with a tubulature for the insertion of a thermometer.

(b) TEMPERATURE CORRECTIONS

It is customary to determine the exact length of polariscope observation tubes at the standard temperature of 20° C. The length of any tube at any temperature may be obtained by the following formula:

$$L_t = L_{20}\ [1+\beta\ (t-20°\ \mathrm{C})], \tag{35}$$

where L_{20} is the length at 20° C and β is the coefficient of linear expansion of the material of which the tube is made. For glass, $\beta=0.000008$, and for brass, $\beta=0.000019$. From eq 35 for $L_{20}=200$, $L_{30}=200.016$ for glass and 200.038 for brass. It is evident that the errors resulting from changes in length of tubes of either material are negligible in ordinary use, but it is customary to apply the correction in all precision measurements.

(c) ACCURACY

All types of polariscope tubes are accepted by the Bureau for test. The tolerances adopted by the National Bureau of Standards for polariscope tubes are given in table 8.

TABLE 8.—*Tolerances for polariscope tubes*

Length	Tolerance
mm	*mm*
400	±0.04
200	±.03
100	±.03
50	±.03
25	±.03

2. COVER GLASSES*

Glass which is not free from strain is doubly refractive, and on this account should not be used between the polarizing and analyzing systems of a polariscope. It is therefore of great importance that cover glasses be made of optical glass and thoroughly annealed. A strain in the cover glass is in effect a rotation, a cause of many baffling discrepancies that occur in polarizations. There is no infallible method of detecting this trouble after the glass is in use, the only safe procedure being to use cover glasses which have been tested, and to put as little pressure as possible on the screw caps. After a setting has been made, it is advisable to rotate the tube in the trough of the instrument; if the halves of the field show variations in intensity, strain exists in one or both of the glasses. Strains may be caused by poorly fitting rubber washers. These should be made from the best quality rubber, soft and flexible. They should be made of such size that they lie flatly and evenly in the cap with no marginal elevation. Once a glass has been strained, it should not be used for several days or until test shows the absence of strain. All cover glasses must have plane, parallel surfaces, free from scratches, and should never be less than 1 mm thick. A thickness of 1.5 to 2 mm is preferable. The necessity for optically perfect glasses has not received the attention its importance demands. The cover glasses used in the laboratories of the National Bureau of Standards for Bates-type polariscope tubes conform to the following specifications:

"Cover glasses shall be made from clear, colorless optical glass, thoroughly annealed, free from strain, and shall show no optical rotation or double refraction when observed in a precision polarimeter. The surfaces shall be plane and parallel and be free from scratches. The edges shall be slightly rounded to prevent chipping. Plane parallelism shall be within 5′; thickness 1.85 ±0.15 mm; diameter 23.2 ±0.2 mm." The National Bureau of Standards will accept polariscope tube cover glasses for test.

3. VOLUMETRIC FLASKS**

(a) SPECIFICATIONS

(1) MATERIAL AND ANNEALING.—The material should be the best quality of glass, transparent, and free from bubbles and striae. It should have small thermal hysteresis and should adequately resist chemical action. All flasks should be thoroughly annealed before being graduated.

(2) DESIGN.—The cross section of the neck must be circular, and the shape of the flask must be such as to admit of complete emptying

*See test fee schedule 423, p. 553.
**See test fee schedule 241, p. 558.

and drainage from the whole interior surface at the same time. The bottom of the flask should be slightly concave upward and should be of sufficient size to enable the flask to stand on a surface inclined at an angle of 15° to the horizontal. The neck must be cylindrical for at least 1 cm on each side of every graduation mark, but may be enlarged in the form of a bulb between graduation marks (for example, Giles flasks). At the graduation mark the inside diameters of the neck of the flask must be within the limits given in table 9.

TABLE 9.—*Diameters of necks and tolerances for volumetric flasks*

Capacity of flask up to and including—	Diameter of neck		Tolerance—	
	Maximum	Minimum	If to contain	If to deliver
ml	*mm*	*mm*	*ml*	*ml*
10	--------	--------	0.01	0.02
25	8	6	.03	.05
50	10	6	.05	.10
100	12	8	.08	.15
200	14	9	.10	.20
250	15	10	.12	.25
500	18	12	.15	.30
1,000	20	14	.30	.50
2,000	25	18	.50	1.00

(3) GRADUATION MARKS.—The graduation marks must be of uniform width, finely but distinctly etched, must be perpendicular to the axis of the flask, and must extend completely around the neck. On flasks having a capacity of 100 ml, or less, the graduation mark shall be not less than 3 cm from the upper end, nor less than 1 cm from the lower end of the neck, and on flasks having a capacity of more than 100 ml, the graduation mark shall be not less than 6 cm from the upper end, nor less than 2 cm from the lower end of the neck.

(4) UNIT OF VOLUME.—The unit of volume employed is the liter, which is defined as the volume occupied at the temperature of its maximum density (4° C) by a quantity of pure water having a mass of 1 kg. The water is under a pressure of 760 mm of mercury, and the weighings are reduced to vacuo. The one-thousandth part of the liter, called the milliliter (ml), is also employed as a unit of volume.

(5) STANDARD TEMPERATURE.—Twenty degrees centigrade has been adopted by the Bureau as the standard temperature for volumetric apparatus, and an extra charge is made for testing apparatus for use at other temperatures.

(6) INSCRIPTIONS.—Each flask must bear, in permanent and legible characters, the capacity in liters or milliliters, the temperature at which it is to be used, the method of use, i. e., whether to contain or to deliver, and an identification number. In the case of flasks with stoppers, the stopper must bear the same number as the flask, or, if standard interchangeable grindings are used, they must bear the proper identification marks. A suitable arrangement of the inscription is as follows:

No. 134
Contains
100 ml
at 20° C.

(b) TOLERANCES

The tolerances for flasks of various sizes are shown in table 9.

(1) Precision Stamps.—Flasks tested by the National Bureau of Standards and found to comply with the foregoing specifications will be given the official precision stamp of the Bureau. The stamp consists of the letters "NBS" and the year in which the test is made, surrounded by a circle. Thus for the year 1941 the stamp will be

The stamp will be placed on the neck of the flask, above the graduation mark.

(2) Sugar-Testing Flask (Bates).—The type of flask used in the sugar laboratories of this Bureau and in the United States Customs Service is shown in figure 30, No. 1. It is especially designed for sugar polarizations and is described in the Customs Regulations, 1931, chapter XI, Sampling, Weighing, and Testing of Sugars, Sirups, and Molasses, as follows: "The flasks shall have a height of 130 millimeters, the neck shall be 70 millimeters in length and have an internal diameter of not less than 11.5 millimeters and not more than 12.5 millimeters. The upper end of the neck shall be flared, and the graduation marks shall be not less than 30 millimeters from the upper end and 15 millimeters from the lower end of the neck." All flasks shall be standardized to contain 100 ml at 20° C. These specifications permit a maximum internal diameter of the neck of 12.5 mm, which exceeds the maximum allowed in the National Bureau of Standards specifications for 100-ml precision flasks by 0.5 mm. However, since the sugar flask is used almost exclusively for polariscopic work, it is tested as precision volumetric apparatus, and if the tests show it to be in accordance in all respects with the specifications given above, it will be given the precision stamp of this Bureau, described under (b) (1) above.

In the Bates type of flask the neck, while smaller than that of the ordinary 100-ml sugar flask, is made slightly larger than the Bureau's requirements for a flask of this size in order that the neck shall not become clogged when the sugar is being introduced into the flask. The upper end is flared to facilitate pouring. The height of only 130 mm minimizes the dilution of the solution by moisture on the upper part of the neck and gives a length which readily permits the flask to be closed with the thumb while the forefinger rests on the bottom, thereby facilitating a thorough mixing by shaking, with no loss by spilling.

(3) Special.—A number of flasks designed for special purposes are shown in figure 30.

Flask 1 is the Bates-type sugar flask, specifications of which are given above. This flask is used extensively in the United States Customs Service and elsewhere in routine sugar analysis.

Flask 2 is the Kohlrausch flask with a funnel neck to facilitate the transfer of the solid sugar without loss.

Flask 3 is typical of the double-graduated flasks and is used in inversions and clarification methods where one volume is to be diluted to a different volume. The usual sizes are 50–55, 100–110, 200–220, and 500–550 ml.

Flask 4 was designed at the National Bureau of Standards for precision work. The inside diameter of the neck is 5 to 6 mm. The enlarged portion of the neck permits complete mixing of the contents of the flask without the solution coming in contact with the grinding or the thumb until the mixing is complete. Before making to volume, the bulb is dried inside by a current of filtered air. The glass tube is ground to fit the grinding of the flask and also the glass stopper of the tubulated water-jacketed polariscope tube, which permits the transfer from flask to polariscope tube without exposure to the air and the consequent evaporation of the solution. In addition to the 100-ml mark on the neck of the flask, there are supplementary graduations above and below the mark. With this flask it is possible to

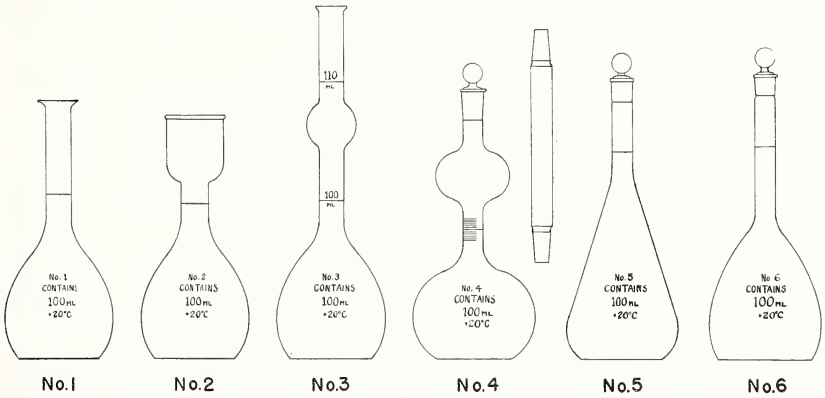

FIGURE 30.—*Volumetric flasks.*

make the calibration and reproduce the volume of solution with an accuracy of 0.002 ml.

Flasks 5 and 6 are special flasks used chiefly in the determination of the density of molasses and sirups.

(4) CORRECTION TABLES.—Tables 106 and 107, p. 612, are given for the convenience of those who wish to verify the graduation of volumetric apparatus. More complete data for this purpose will be found in National Bureau of Standards Circular C19.

4. THERMOMETERS*

(a) GENERAL

Thermometers [1] should be of good design and workmanship and should be made of suitable materials, with special attention to the thermometric properties of the glasses used. Detailed specifications, covering the necessary items for the various types of thermometers suitable for use in polarimetric measurements, have been prepared and are available upon request. A sample form of the specifications is printed in this circular, page 382.

*See test-fee schedule 311, p. 554.

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Mercury-in-glass thermometers are calibrated to agree as closely as possible with the International Temperature Scale adopted in 1927 and now in general use. On this scale, which conforms with the Centigrade Thermodynamic Scale as closely as possible with present-day knowledge, temperatures in the interval −190° to 660° C are defined in terms of the resistance of a standard form of platinum resistance thermometer calibrated at basic fixed points. The International Temperature Scale is defined in NBS Research Paper RP22 [2].

It is highly desirable that a fixed point appear on the scale of a mercury-in-glass thermometer. The ice point (0° C or 32° F) or steam point (100° C or 212° F) is convenient. The volume of the bulb of a mercury-in-glass thermometer is known to change with time and use by amounts which must be taken into consideration if the best results are to be obtained. By checking the fixed-point reading from time to time, these changes may be determined and allowed for. For example, if the ice-point reading is found to be higher or lower than the previous reading, all other readings on the thermometer will be higher or lower by the same amount.

Thermometers provided with graduated metal backs should, in addition, have graduations engraved on the glass stem. The thermometer should be securely and firmly fastened to the back. If the thermometer is of the inclosed-scale (Einschluss) type, such fiducial mark should be placed on the outer glass tube.

Thermometers should comply in all respects with the applicable specification.

(b) ICE BATHS [3]

Because of the changes in bulb volume, the ice bath, which provides a convenient means of determining the amount of such changes, is very important. The most convenient form consists of a wide-mouthed thermos bottle or Dewar flask, filled with a mixture of shaved ice and distilled water, or water obtained by the melting of the ice. Other containers may be used, but are likely to be less convenient because of the more rapid melting of the ice. Clear ice is considered sufficiently pure for the purpose and is readily obtainable. The ice may be shaved by means of a small plane, resembling a carpenter's plane, or other appropriate mechanism. There should be enough water in the mixture to make it soft or slushy, but not enough to cause the ice to float. Excess water which accumulates may be conveniently removed by means of a glass siphon, ending in a rubber tube with a pinch cock. Precautions should be taken to wash the ice and to avoid contaminating it in handling.

5. WEIGHTS*

(a) SUGAR

It is generally advantageous to have special 26- and 13-g weights for weighing out sugar samples for direct polarization. For this work, the Bureau recommends that the ordinary screw-knob type of weight be avoided in favor of a strictly one-piece weight in which the knob forms an integral part of the weight. Gold- or platinum-plated Tobin bronze weights have been found satisfactory. Recently,

*See test fee schedule 226, p. 557.

stainless-steel weights have been introduced, and the indications are that they will prove satisfactory if made from steel of the proper composition. The working standards should conform to the Bureau's requirements for class *B* and the reference standards (i. e., those used only for checking the working standards) should conform to the requirements of class *A*. The maximum error allowed in both classes is 2 mg on the 26-g weight and 1.5 mg on the 13-g weight.

(b) ANALYTICAL

In most analytical procedures in the sugar laboratory, a good grade of analytical weights should be accurate enough, but it is not safe to rely on them unless they are tested. For work requiring considerable accuracy in the weighing, the weights should conform to the Bureau's requirements for class *S*. The maximum errors allowable range from 0.5 mg on the 100-g weight to 0.1 mg on the 1-g weight and 0.02 mg on the 10-mg weight. For less accurate work, weights conforming to the requirements of class *S*2 having allowable errors of five times those of class *S*, may be used.

(c) REFERENCE STANDARDS

Weights are liable to change. They cannot be used without a certain amount of wear, which will ultimately make an appreciable change in their values. Ordinary analytical weights sometimes suffer serious change from the oxidation of adjusting material placed in the cavity under the knob. Weights must therefore be retested from time to time according to the nature of the weights and of the work for which they are used. Reference standards are therefore needed, since it is seldom advisable to send the weights to this Bureau as often as would be needed. There is no gain in the purchase of complete sets for this purpose when this is done at the expense of quality, as must usually be the case. A set of working standards can be tested readily by intercomparison of the weights among themselves, if one or two reference standards are available on which to base the calibration. The Bureau will furnish information in regard to series that are much better than the ones generally used and yet involve no great amount of additional labor. Probably the best denominations for reference standards would be one 100- or 50-g weight, one 1-g weight, one 10-g weight, one 26-g weight, and one 13-g weight. The 1-g weight should be made of platinum, as it is the starting point for the determination of the milligram weights.

For the best reference standards, the Bureau recommends one-piece weights. Gold- or platinum-plated Tobin bronze weights are the most satisfactory ones now available for this purpose for weights above 1 g. Weights having a hard metal driven plug would rank next. Standards for the analytical sets should conform to the requirements for class *S* and be tested under that class.[5] Reference standards for the "sugar weights" should come under class *A*, as stated above.

(d) CERTIFICATION

Sugar weights and analytical weights are among the weights tested by the Bureau, but the rougher weights are not regularly accepted for test.

[5] The same kind of weights, but less accurately adjusted, may be obtained as class *A* and class *B* weights. For extreme accuracy (seldom, if ever, needed in weighings for polarimetry), when careful corrections must be made for the buoyant force of the air, only one-piece weights can be relied upon, and the volume of each weight must be determined. This requires that the weights come under class *M*.

Information as to the precision to which corrections will be certified for weights of classes *A*, *M*, or *S*, and lists of tolerances for any class, will be supplied on application to this Bureau. Full details as to specifications, tolerances, and precision of corrections, together with other information as to standard weights and some of the methods of testing them, are given in National Bureau of Standards Circular C3.

To assist in the identification of the weights, the test number assigned to the weights by the National Bureau of Standards will be stamped on the bottom of the box provided for keeping them, thus NBS Test No. 4978.

The shipping case or the inner wrappings will always be sealed when tested weights are shipped from the Bureau.

(e) SUBMISSION OF WEIGHTS FOR TEST

A written request for the testing should be sent when the weights are shipped. This should always indicate the class of weights submitted, and if two different tests are available in that class, the character of test desired. Sufficient information should also be given to enable the Bureau to identify the package.

If weights have already been used as standards in exacting work, and it is important to know what their corrections were at the close of such work, this fact should be stated; otherwise, weights are carefully cleaned before being tested.

Weights should be packed tightly. Sets in covered cases generally need extra packing inside the case. The very small sheet-metal fractional weights are especially likely to work out of place and be damaged.

Address packages and correspondence, "National Bureau of Standards, Washington, D. C."

6. BALANCES

The methods of analysis employed in the sugar laboratory require the use of a high-grade analytical balance for such operations as the determination of ash, moisture, and specific rotation, as well as a special sugar balance for the rapid weighing of sugars, molasses, and sirup for the usual saccharimetric determinations.

In selecting an analytical balance, it is well to keep in mind several essential points. The sensibility of the balance is influenced by (1) distance between the center of gravity and the point of support, (2) coincidence of the planes of the three surfaces on which the three knife-edges bear, (3) length of the arms of the beam, and (4) reduction of friction to a minimum by finely ground and polished knife-edges and planes. In addition, the sensibility is affected by the weight of the beam; in general, a balance with a light beam is more sensitive than one with a heavy beam.

The Bates sugar balance, especially designed at the National Bureau of Standards for saccharimetric work, has a number of improved features. The customary bows supporting the pans have been replaced by single-arm hangers at the back, an arrangement which gives free access to the pans and reduces to a minimum the danger of spilling sugar on the pans. The weighing scoop is adjusted to balance exactly either of the pans, thereby avoiding the use of a counterpoise weight.

The errors introduced by evaporation or absorption of moisture during weighing are greatly reduced by the rapidity of weighing with this balance. The general design and construction of the balance is such as to make it especially adapted for use in the tropics. It has a capacity of 200 g, with a sensitivity of 1 mg, which may be increased to 0.2 mg by raising the center of gravity weight on the pointer.

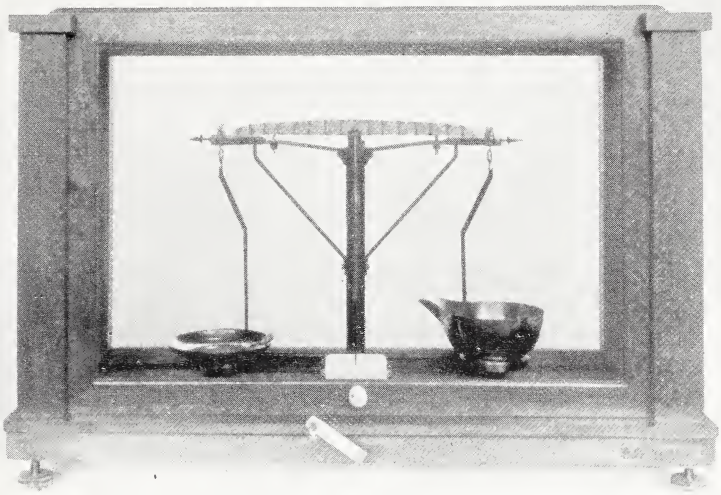

FIGURE 31.—*Bates sugar balance.*

7. REFERENCES

[1] NBS Circular C8, Testing of Thermometers (current edition).
[2] G. K. Burgess, BS J. Research **1**, 635 (1928) RP**22**.
[3] E. F. Mueller and R. M. Wilhelm, Proc. Am. Soc. Testing Materials **38**, pt. 1 (1938).

PART 2. RAW AND REFINED SUGARS AND SUGAR PRODUCTS

VII. POLARIZATION OF RAW AND REFINED SUGARS

1. SAMPLING AND MIXING OF SAMPLES

The importance of a correct method of sampling raw sugar cannot be overestimated. If this step is carelessly or erroneously carried out, the most careful work on the part of the chemist is vitiated. The details of the process of sampling should be arranged with two requirements kept in view: (1) The sample should be thoroughly representative of the package, and (2) after the sample is taken, it should undergo no change until used for analysis.

In order to obtain a representative sample, the sampling instrument, called the trier, should be plunged into the middle of the package and drawn out filled with sugar. If the trier has the correct length and the sampling is skillfully done, all the layers of sugar in the package are represented in the sample. Great care should be exercised to avoid taking a surface sample, since the variations caused by drying or absorption of moisture have their maximum effect at the surface. The dimensions of sugar triers are given in the regulations of the United States Treasury Department relative to sampling of imported sugars. These regulations are printed beginning on page 781 of this Circular.

If the sugar is contained in barrels or other wooden packages, it should be sampled by running the "long trier" or "barrel trier" diagonally through the package from chime to chime. In case molasses has drained to the bottom of the package, especial care must be taken to obtain the sample symmetrically.

In procuring samples from large shipments of sugar, it is advisable to take samples from every package, to mix the large quantity of material thoroughly, and to resample the mixture for analysis.

In order to prevent a change in the composition of the sample taken, the total contents of each trier should be emptied into a tightly covered receptacle and the trier left clean for the next sample, the whole operation being completed within a few seconds. The subsequent mixing and resampling should be conducted in such manner as to avoid unnecessary exposure to the atmosphere. These precautions are necessary because of the great tendency of raw sugar to change its moisture content when exposed to the air.

A large proportion of the impurities in raw sugar is in the form of molasses clinging to the surfaces of the crystals, and the evaporation or absorption of moisture may be very rapid. The action of an absorbing material during mixing (such as the brown paper frequently used) may affect the polarization very markedly by wiping the molasses from the surfaces of the crystals. If samples are to be pre-

served before analysis or for subsequent reference, they should be placed in tightly sealed containers in order to avoid loss by evaporation.

Further details as to the correct procedure in sampling will be found in the United States Treasury Customs Regulations, page 786.

2. DIRECT POLARIZATION

The determination most widely used in the analysis of sugar and sugar products, both in chemical control during extraction and refining and also in the adjustment of commercial transactions, is the direct polarization. The term "direct polarization" is defined as the reading on the saccharimeter of 26.000 g of the sample dissolved in 100 ml of solution at 20° C, with only such substances removed by clarification as impede the passage of light. The value thus obtained is the resultant optical rotation of all optically active substances present in the solution and indicates the percentage of sucrose only in cases where the other constituents have no effect on the rotation. Distinguished from the direct polarization, is the Clerget, or double-polarization, method, which indicates the true percentage of sucrose. In sugars of high purity, the direct polarization and the sucrose by the Clerget method give results that closely agree, but in low-grade sugars and molasses the differences may become considerable.

The direct polarization is executed in a great variety of ways with respect to the details of manipulation. The following method is the one most conveniently used in commercial work, and if carefully performed, the results are sufficiently uniform and reproducible for the adjustment of sugar trade relations and for the control of sugar manufacture in the sugar industry.

The sample is thoroughly mixed, all lumps being broken up, and weighed very quickly in the weighing dish, great care being taken to prevent moisture change during weighing, by hastening the process as much as needed accuracy permits. (If the polariscope is read to only 0.05° S, it is useless to weigh more closely than 0.015 g). By means of a jet of distilled water, the sample is then washed into a 100-ml sugar flask and dissolved. This is readily accomplished after a little practice. However, if difficulty is experienced, the transference to the flask may readily be made by use of a funnel, the stem of which extends just into the body of the flask. The sugar is then brought into solution by a few minutes shaking, a shaking machine being convenient if large numbers of samples are to be handled. After solution is complete, the clarifying agent is added. The method of clarification depends on the nature and amount of impurities present. The universal principle is to add the minimum quantity necessary to clarify, whatever the agent added. In a large proportion of samples the clarification consists in the addition of 0.5 to 2 ml of basic lead acetate solution. The contents are mixed and the volume completed to 100 ml, the neck of the flask being washed down. If foam appears on the surface of the meniscus, rendering it impossible to adjust the volume accurately, it may be dispersed by blowing upon it a small quantity of alcohol or ether from an atomizer.

To obtain good definition while making up to volume, the bottom of the meniscus should be made to appear dark by a reflection of the finger or of a section of rubber tubing placed a few millimeters below the mark on the neck of the flask. The meniscus, shaded in this way,

should be made tangential to the upper edge of the graduation mark. It is essential that the temperature of the solution during the process be the same as that of the saccharimeter, tubes, and quartz control plates.

The solution is then shaken thoroughly and the entire contents of the flask is poured on a filter in a stemless funnel. The first 25 ml of the filtrate is rejected, since this portion is almost invariably made turbid by the passage of a small amount of the lead precipitate through the filter paper. In addition, the first portions passing through the dry filter paper suffer a change in concentration, as shown by Hardin and Zerban [1]. By rejecting the 25-ml portion, this absorption effect is largely or wholly avoided. During the filtration it should be made an invariable practice to cover the funnels with cover glasses to pre-

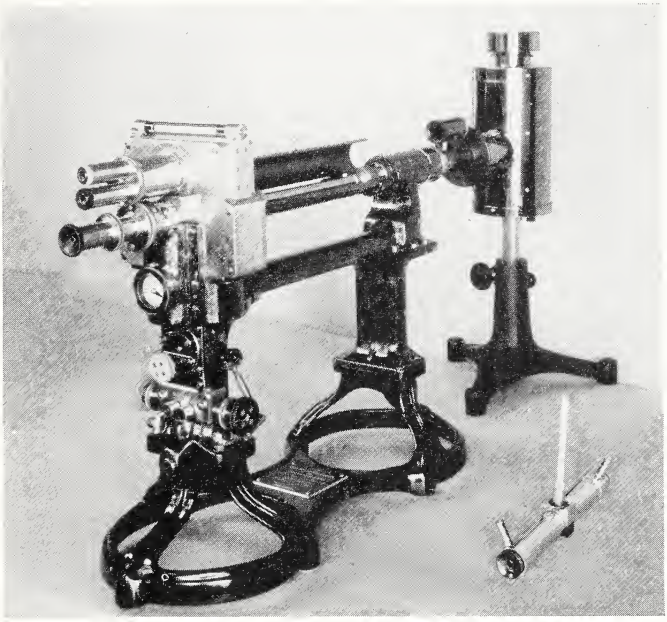

FIGURE 32.—*Bates saccharimeter and lamp.*

vent evaporation of the solution. This important precaution is frequently neglected. The contention that the evaporation is one of the constant errors of this method is not valid. The evaporation is not constant but depends on the accidental conditions of temperature, relative humidity of the atmosphere, and the movement of air in the room. Bates and Phelps [2] have made an exhaustive study of the influence of atmospheric conditions in the testing of sugars. They found for raw sugars, filtered once, that:

1. The increase in the polarization due to evaporation is negligible in ordinary testing for all potential heads ($P_s - P_a$) up to 22 mm, and that it is therefore unnecessary to use any precautions to prevent or to correct for evaporation for ordinary atmospheric conditions, provided the duration of the filtration does not exceed 10 or 12 minutes.

2. If the correction for the increase in polarization is desired, it may be obtained from the following equation:

$$Q=0.00017(P_s-P_a)T, \tag{36}$$

where Q=increase in polarization in degrees sugar,
Ps=saturation vapor pressure at the temperature of the solution,
Pa=saturation vapor pressure at the temperature of the dew point in the air,
T=time of filtration in minutes.

Q should be subtracted from the observed polarization to obtain the true polarization.

3. Practically all increase in polarization, regardless of atmospheric conditions, may be prevented by covering the funnel with a watch glass.

When all or a part of the filtrate is returned to the filter, the concentration is increased, since this filtrate takes up the solution already

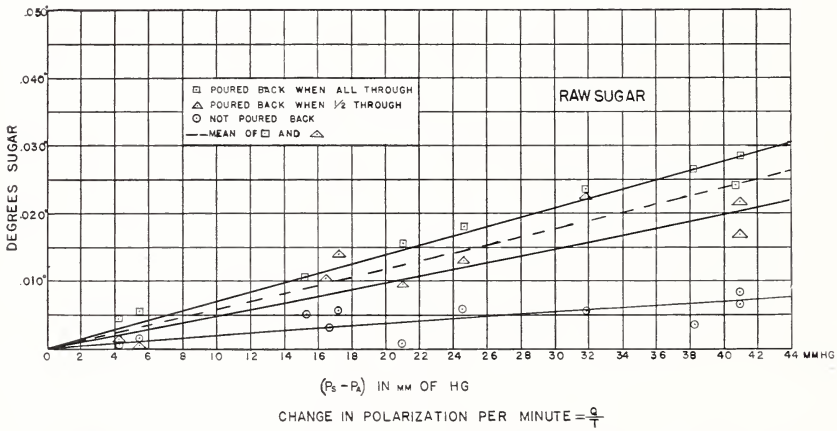

FIGURE 33.—*Curves showing the effect of evaporation on the polarization of raw sugars.*

adhering to the filter paper and which has become concentrated by evaporation after the level of the solution in the funnel has fallen. Bates and Phelps show graphically in figure 33 the change in polarization per minute when normal solutions of raw sugars are poured back after filtration.

Before filling the polariscope tube, it is rinsed two or three times with the filtered solution. During the rinsing the filtration cylinder should be given a rotary motion to stir its contents. This stirring brings the solution to a uniform density, thereby permitting a sharp focusing of the eyepiece of the saccharimeter. Care should be exercised to avoid errors due to the physical condition of the tube.

The accepted reading of the saccharimeter scale should be the average of at least three settings of the end point, and it is a great advantage to use both eyes in making the observations.

Direct polarization by this method gives a value which is uniformly reproducible. It does not, however, represent the percentage

of sucrose in raw sugars, because it does not take into account other optically active substances which are usually present.

3. CLARIFICATION

(a) GENERAL

All methods of clarification at present available have accompanying disadvantages which necessitate great precautions in order to minimize their effect.

The choice of a clarifying agent for polariscopic work depends largely on the color of the sample to be tested. Agents in most frequent use are alumina cream, basic lead acetate, and decolorizing carbon. In less frequent use, but having some advantages in special cases, are neutral lead acetate, basic lead nitrate, alum, sodium hydrosulfite, and sodium hypochlorite.

(b) ALUMINA CREAM

Alumina cream is a suspension of aluminum hydroxide $Al(OH)_3$ in water. It is prepared by precipitation from alum or aluminum sulfate solution by means of ammonia. The precipitate is washed free of soluble salts or left unwashed, depending on the use to which it is to be put.

In case the precipitate is to be washed, it is advisable to add the ammonia in slight excess. The washing of the precipitate may be conveniently carried out by suspending the mixture in parchment-paper bags in a vessel of water, changing the water in the vessel frequently, or it may be washed in the usual way on a filter, provided caution is used to prevent the precipitate from becoming dry. The washing is continued until a portion of the wash water tested with barium chloride shows only traces of dissolved sulfates. The washed alumina cream may be used either as the sole clarifier for high-grade samples, if its action is sufficiently effective, or it may be used in conjunction with basic lead acetate. When used with lead, it increases the clarifying action of the basic lead acetate and permits the use of a smaller quantity than would otherwise be necessary. When the washed alumina cream is used alone, the only error introduced is caused by the volume of the precipitate of aluminum hydroxide. If only a few milliliters is used, the volume of the dry solid is small, and for all ordinary purposes, negligible.

If the alumina cream contains an excess of alum and other soluble sulfates, its use is recommended by many as an aid to clarification by basic lead acetate in the analysis of very impure products where a large quantity of lead acetate is required. The alumina cream then fulfills several purposes. It precipitates the excess of lead as lead sulfate. It adds its own clarifying effect and tends to furnish a slightly acid solution, which decomposes some of the compounds formed by lead with some sugars, notably levulose.

Impure saccharine products usually contain large quantities of dissolved inorganic salts, so that the addition of a clarifier containing a relatively small quantity of soluble salts is not seriously detrimental.

The method of preparation of the Association of Official Agricultural Chemists [3] is as follows: Prepare a cold saturated solution of alum in water. Add ammonium hydroxide with constant stirring

until the solution is alkaline to litmus, allow the precipitate to settle, and wash by decantation with water until the wash water gives only a slight test for sulfates with barium chloride solution. Pour off the excess of water and store the residual cream in a stoppered bottle.

(c) BASIC LEAD ACETATE

(1) Preparation.—Basic lead acetate is the clarifying agent most extensively used. It is formed by the chemical combination of normal

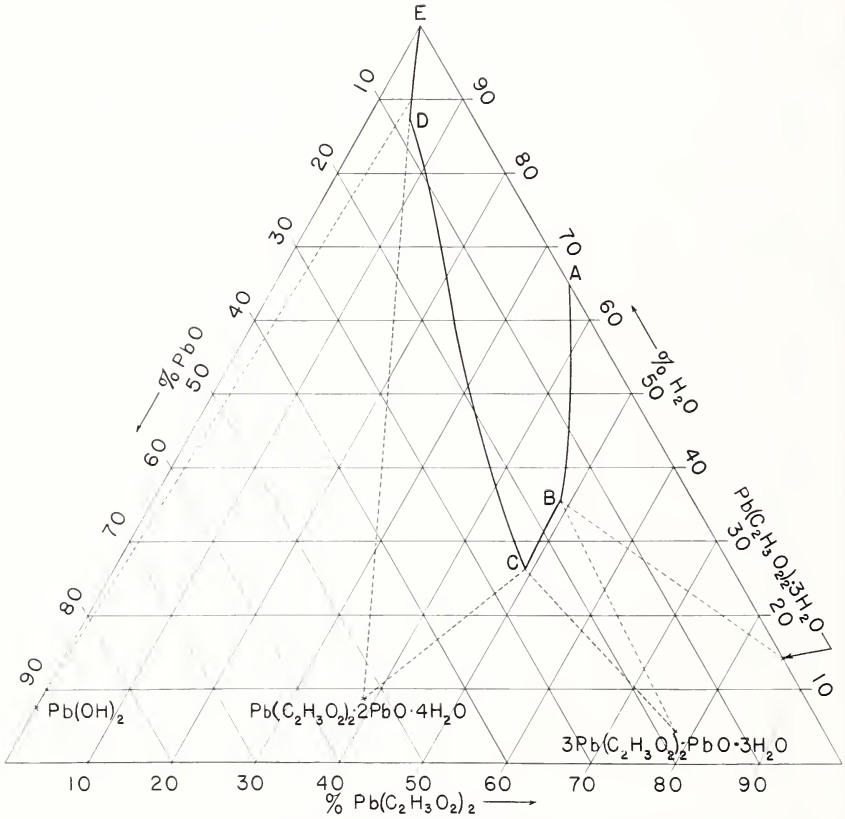

Figure 34.—*Isothermal equilibrium between lead acetate, lead oxide, and water at 25° C.*

lead acetate, $Pb(C_2H_3O_2)_2$ with litharge, PbO. Jackson [4] in a study of the equilibrium in the system lead acetate, lead oxide, and water, has shown that four compounds capable of existing in the solid phase are *neutral lead acetate*, $Pb(C_2H_3O_2)_2.3H_2O$; *tetra-lead-monoxy-hexacetate*, $3Pb(C_2H_3O_2)_2$ $PbO.3H_2O$; *tri-lead-dioxy-diacetate*, $Pb(C_2H_3O_2)_2 2PbO.4H_2O$; and *lead hydroxide*, $Pb(OH)_2$. The basic lead acetate of commerce is a mixture of the two basic acetates, $3Pb(C_2H_3O_2)_2.PbO$ and $Pb(C_2H_3O_2)_2.2PbO$. The reagent known as Horne's dry lead has been found to be quite uniform in composition. It consists of a mixture corresponding to 4 parts of $3Pb(C_2H_3O_2)_2PbO$ and 3 parts $Pb(C_2H_3O_2)_2.2PbO$. At this Bureau it has been found

advisable to use this product for preparing the clarifying solution, as well as for dry lead clarification, by the Horne method [5].

The laboratory method of preparing the solution prescribed by the Association of Official Agricultural Chemists [3] is as follows:

Boil 430 g of neutral lead acetate, 130 g of litharge[6] and 1 liter of water for 30 minutes. Allow the mixture to cool and settle, and then dilute the supernatant liquid to a specific gravity of 1.25 with recently boiled distilled water. Solid basic lead acetate may be substituted for the normal salt and litharge in the preparation of the solution.

In 1909 The International Commission for Uniform Methods of Sugar Analysis, adopted the solution of basic lead acetate of the German Pharmacopoeia, which is prepared by boiling 3 parts normal lead acetate, 1 part lead oxide, and 10 parts of water. Various other proportions of lead acetate and lead oxide for the preparation of the reagent are given in various handbooks.

With the exception of the dry basic lead acetate prepared by a few firms, the samples occurring in commerce and also samples prepared in the laboratory, even by official methods, vary in composition within wide limits. Basic acetates having the highest proportion of PbO have the greatest clarifying power, but they also combine to the greatest extent the errors accompanying clarification with this reagent.

The constitution of basic acetate may be determined chemically by a double analysis of the sample.

(2) Analysis.—Weigh out 10 g of the solid or take a known volume of the solution containing approximately this quantity of the solid substance, and dissolve in water in a 500-ml flask. In general, this will give a milky solution because of the partial hydrolysis of the lead salt. In order to avoid the possibility of the subsequent formation of basic lead sulfate, it is advisable to add a measured volume of normal acetic acid until a clear solution is obtained. Then add the equivalent of 60 ml of normal sulfuric acid, fill to a volume of 501.3 ml, close the flask, shake thoroughly, and allow the precipitate to settle. The extra 1.3 ml is to compensate for the volume of the precipitated lead sulfate, and is added from a burette after filling the flask to the 500-ml mark.

After the precipitate has settled, determine the excess of sulfuric acid by adding a slight excess of barium chloride to 100 ml of the clear solution. Filter the precipitate, ignite, and weigh as barium sulfate. The calculation of the total lead present computed as lead oxide is as follows:

$$5\left[\text{ml } H_2SO_4 \times \text{normality factor} - \frac{\text{wt. } BaSO_4}{1/2 \text{ mol. wt. } BaSO_4}\right] 1/2 \text{ mol. wt. PbO}$$

$$\text{or } 5.578\left[\text{ml } H_2SO_4 \times \text{factor} - \frac{\text{wt. } BaSO_4}{0.1167}\right]$$

To ascertain the quantity of lead present in the form of $Pb(C_2H_3O_2)_2$ and that in the form of PbO, add to another 100-ml aliquot portion a few drops of phenolphthalein and titrate with a standard caustic alkali solution, taking the necessary precautions to free the solution of carbonic acid. The calculation of PbO is as follows: 5(total ml of normal acid added—ml of normal alkali) 1/2 mol. wt PbO.

[6] Directions for the preparation of activated litharge are given under (i)(1) p. 237 this Circular.

The total normal acid is the sum of the acetic and sulfuric acids. This computation gives the weight of lead present as lead oxide. If this is subtracted from the total lead oxide, the remainder is the lead oxide present in the form of neutral acetate, and this weight multiplied by the factor 1.4574 reduces it to the weight of neutral acetate.

Basic lead acetate has the great advantage of efficiency, but it has also many disadvantages which require the exercise of great caution in its use. In general, the minimum quantity which is necessary to clarify the solution should be used. This quantity is gaged with requisite accuracy by experienced workers. The needed quantities for particular cases cannot be stated, but the following approximate numbers are given as examples: For Java, Peruvian and Cuban "first" sugars, from 0. 5 to 2 ml of the lead solution; molasses sugars, 2 to 4 ml; Philippine III, 3 to 6 ml. Molasses usually requires 6 to 12 ml. Many analysts follow the lead treatment by adding a little alumina cream. The washed alumina cream is used for high-grade samples, the cream with soluble sulfates for low-grade samples.

(3) Correction for Volume of Precipitate.—The basic lead acetate owes its clarifying action to its ability to precipitate the suspended albuminoids along with other organic impurities. Since the total volume of 100 ml is occupied by the solution and precipitate, the solution alone occupies somewhat less than the volume indicated and is thus correspondingly concentrated. The error in the polarization thus caused has occasioned considerable discussion, and a number of methods have been devised either to correct or to avoid it.

Method of Sachs. [6].—This is practically a direct measurement of the volume of the precipitate. It is described in the Spencer-Meade Handbook [7] as follows: Clarify 100 ml of the juice or the dissolved normal weight with the subacetate as usual. Wash the precipitate by decantation, first with cold water and finally with hot water until all of the sucrose is removed. Transfer the precipitate to a 100-ml flask and add one-half the normal weight of cane sugar (of known polarization), dissolve the sugar and dilute the solution to 100 ml; mix, filter, and polarize, using a 400-mm observation tube.

The volume of the precipitate is $(100P'-100P)/P'$, in which P is the polarization of the sugar taken, and P' the polarization of the sugar in the presence of the precipitate.

Method of Scheibler. [8].—To 100 ml of the sugar solution 10 ml of lead solution is added and the saccharimetric reading taken. A second solution is prepared by mixing the same volumes of the saccharine liquid and lead solution, which is then diluted to 200 ml and polarized.

The Scheibler method may be expressed by the following equations: $r=100R/(100-A)$, where r is polariscopic reading, R the true reading if the solution were continued in 100 ml, and A the volume of the precipitate. Similarly, $r_1=100R/(200-A)$. Combining the two equations and eliminating A, we obtain $R=rr_1/(r-r_1)$. A further simplification is due to C. A. Browne, who deduces the expression $R=4r_1-r$.

Method of Horne.—The following method gives a more direct determination of this volume and is free from the difficulty of determining small differences between large numbers. A solution of the raw sugar is prepared and precipitated in the usual manner. The precipitate is allowed to settle and is washed by decantation, all the

washings being poured through a weighed Gooch crucible. As little of the precipitate as possible is transferred to the filter. When the washing is completed, the precipitate is transferred to a weighed picnometer, which is filled to the mark and weighed. The difference between the first and final weighings gives the total weight of the lead precipitate.

The density of the precipitate is found in the following way:

Let c=weight of precipitate transferred in decanting,

A=weight of water in picnometer when filled,

B=weight of water and precipitate in picnometer,

C=weight of precipitate in picnometer found by difference between second and third weighing of Gooch crucible,

$C+W$=total weight of precipitate, and

Density$=C/A-(B-C)$.

The total volume of the precipitate is then its total weight divided by its density, thus

$$\text{Volume}=W/D=\frac{C+c}{C}/[A-(B-C)].$$

If care is taken to avoid any considerable loss of precipitate during the decantation, the determination may be shortened by neglecting the small quantity of precipitate lost in this way. The washed precipitate may be transferred directly to the picnometer, which is filled and weighed. The picnometer is then emptied directly upon a weighed Gooch filter. The volume of the precipitate is then the weight of water displaced in the picnometer by the precipitate, or $A-(B-C)$. If the weight of the precipitate lost in the decantation does not exceed a few percent, the shorter method is satisfactory.

Horne dry-lead method.—A method intended to avoid rather than correct for the effect of the volume of the lead precipitate has been proposed by Horne [5]. Dissolve the sample in water and make up to 100 ml before adding the clarifer. Add a minimum quantity of dry basic lead acetate until sufficient clarification is obtained. Or, as in careful work with a lead solution, add the solid in successive small amounts until precipitation is almost complete. It is evident that it is necessary to stop short of complete precipitation because an excess of the solid, which does not produce a corresponding precipitate, serves to swell the volume of solution and a corresponding error is introduced. Horne has been able to show that by this method the volume of the solution is very approximately that indicated.

(4) Effect on Sucrose.—It is often erroneously stated that basic lead acetate has no effect on the rotation of sucrose. The experiments of Bates and Blake [9] show that errors in rotation caused by excessive amounts of basic lead acetate solution are of equal importance to the other errors in saccharimetry. These authors have found, figure 35, that an excess of ½ ml causes a diminution of polarization of 0.10° S; 1 ml, 0.12° S; 2 ml, 0.11° S; 3 ml, 0.09° S. The rotation reaches a minimum value when an excess of 1 ml is present. It returns to its initial value when 6 ml in excess has been added and continues to increase linearly with the amount of lead solution added. If as much as 50 ml is present, the rotation is then increased by a whole degree Ventzke. This source of error is avoided if the minimum quantity of lead solution necessary to clarify is added.

(5) Effect on Levulose.—By the action of basic lead acetate on levulose, the direct polarization may be considerably disturbed. This effect may occur from two causes. A soluble combination of lead and levulose may be formed which has a lower specific rotation than levulose or the lead-levulose compound may be actually precipitated from solution. The result in either case is an increase in dextrorotation or a higher polarization. Prinsen Geerligs has shown that basic acetate of lead precipitates levulose when the same solution contains salts which are capable of producing insoluble compounds with lead.

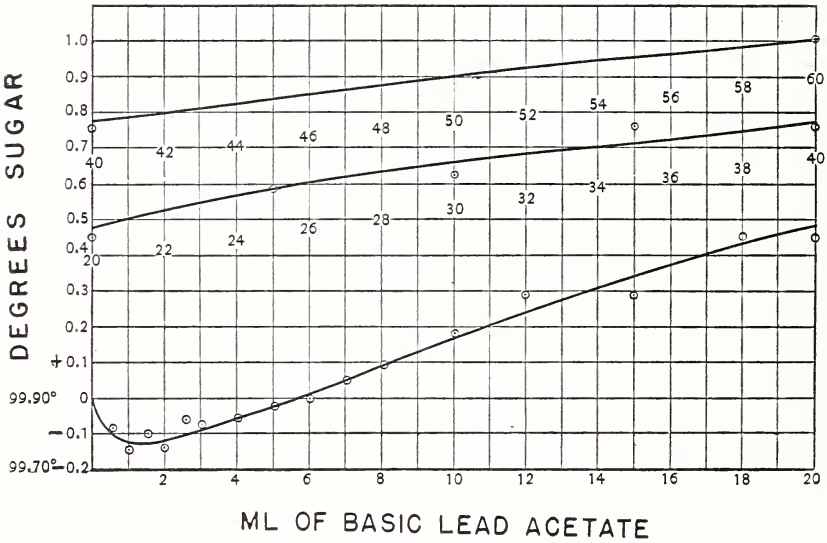

Figure 35.—*Influence of lead acetate on normal sugar solution.*

The combinations between lead and levulose are very easily broken up by a slight acidification. Acetic acid is sufficiently effective, but many other acids have been used for this purpose. Sulfur dioxide, tannic acid, and, as is frequently claimed, a solution of alum is acid enough to decompose this rather loose combination. In any case, only a slight excess of acid should be present.

(d) BASIC LEAD NITRATE (HERLES SOLUTION)

Herles solution [10] is prepared by dissolving 100 g of solid NaOH in 2 liters of water, and a second solution is prepared by dissolving 1 kg of neutral lead nitrate in 2 liters of water. Upon mixing equal volumes of the two solutions, basic lead nitrate is precipitated, the reaction being expressed by the equation

$$2Pb(NO_3)_2+2NaOH=Pb(NO_3)_2.Pb(OH)_2+2NaNO_3.$$

The precipitate is washed free of soluble impurities and mixed with water to a cream for use in clarification. The clarification may also be performed by forming the basic lead nitrate in the solution to be polarized. This is done by first adding a measured quantity of the above lead nitrate solution, 1 to 10 ml, according to the darkness of the sample, and then, after mixing, adding an exactly equal quantity

of the alkaline solution. An excess of alkali must be avoided. The mixture is then shaken and made to volume. The latter procedure gives the better clarification but introduces a considerable quantity of soluble salts, which may affect the polarization. The defects of the basic nitrate are, in general, those of the basic acetate. The volume of the precipitate is even greater because of the bulk of the solid clarifier. The precipitation of reducing sugar is even more marked than in the case of the basic acetate.

(e) HYPOCHLORITE (ZAMERON METHOD)

The hypochlorite solution is prepared by grinding 625 g of dry bleaching powder in a mortar with 1 liter of water. The mass is squeezed out in a sack and the extract filtered through paper. The filtered solution, about 700 to 800 ml of about 18° Baumé, is preserved in a stoppered dark-glass bottle in darkness. To perform the clarification, a few milliliters of the hypochlorite solution is added to the sugar solution and then a few milliliters of neutral lead acetate solution. The reagent usually causes a slight rise in temperature so that the solution should be readjusted to the temperature of the polariscope before making to volume. This method of clarification is very effective, and if no great excess of the reagent is employed, the reducing sugars are unaffected. The volume of the precipitate, which is increased because of the presence of insoluble lead chloride, is the main fault of this method.

(f) HYDROSULFITE

Sodium hydrosulfite is prepared by the reaction of zinc, sodium bisulfite, and sulfuric acid according to the formula

$$2NaHSO_3+Zn+H_2SO_4=ZnS_2O_4+Na_2SO_4+2H_2O.$$

The zinc hydrosulfite is changed to the sodium compound by the reaction

$$ZnS_2O_4+Na_2CO_3=Na_2S_2O_4+ZnCO_3.$$

The sodium hydrosulfite is salted out from solution by means of sodium chloride and dehydrated by warming with strong alcohol. The compound is then dried in a vacuum at 50° to 60° C. This substance is produced commercially under the names of Blankit and Redo. It is frequently used in sugar manufacture for bleaching massecuites and, in dissolved form, as a wash for whitening sugar in centrifugal machines. To prepare a solution for polarization, a quantity of alumina cream is added and then a few crystals of hydrosulfite, 0.1 to 1 g, according to the color of the solution. The solution is made up to volume, shaken thoroughly, and filtered. As the clarified solutions occasionally redarken, they should be polarized immediately. The clarifying action, according to Weisberg [11], is due to free sulfurous acid and nascent hydrogen. The reduction by the latter leaves compounds which may be reoxidized and cause a redarkening of the solution.

Another hydrosulfite derivative (sodium sulfoxylate-formaldehyde) known as Rongalite accomplishes a permanent clarification but it is slower and less effective than Blankit.

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The defects of hydrosulfite as clarifiers are, in addition to the frequent redarkening, their effect on reducing sugars, the possible separation of finely divided sulfur, and their ineffectiveness in discharging the color of caramel bodies. Bryan [12] states that the rotation of dextrose is lowered by hydrosulfites and finds evidence of the formation of a laevo oxysulfonate. No immediate effect is observable upon sucrose or fructose, but sucrose is apparently inverted by a prolonged action. These clarifiers have not come into general use in analytical work, but nevertheless they are unique in that they produce no volume error.

(g) BONE CHAR

In cases where neither alumina cream nor lead subacetate is capable of producing a clear solution, recourse may be had to bone black. Bone black, for analytical purposes, may be prepared by treating the granular material used in sugar refining with a slight excess of hydrochloric or nitric acid until all of the mineral matter is dissolved. The treated char is washed with boiling water, dried at 120°, and finely powdered and bottled. The more completely the material is freed from mineral matter, the more effective is its action for analytical purposes. Bone black probably owes its clarifying action to the very large surface which is caused by its porosity.

The most serious error accompanying clarification with bone char is caused by its tendency to absorb sugar and thus give abnormally low readings. For this reason, most official methods of clarification exclude bone black as an agent. It is difficult to make a correction for the amount of sugar absorbed, because it varies with the composition and concentration of the sample and the condition of the bone char. In order to avoid the error arising from the absorption of sugar, the absorption coefficient may be determined under the approximate conditions of the analysis or the solution may be made up to volume and filtered through a column of bone black, the first third of the filtrate being rejected.

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VIII. CLERGET METHOD

1. INTRODUCTION

The direct polariscopic reading of a sugar solution is the resultant rotation of all optically active substances present, and is conse-

quently a correct measure of the sucrose only when the other substances present have no effective rotatory power. If other optically active substances are present, the direct polarization must be supplemented by a second observation in which the rotations of these substances are kept constant while that of sucrose is subjected to a change which can be measured and is known to be an exact function of the quantity of sucrose. This change is brought about by the hydrolysis of sucrose to invert sugar. The change of rotation of the normal solution of pure sucrose is known as the Clerget divisor. The divisor is not a constant but its numerical value is influenced by concentration, temperature, and impurities. The hydrolysis or inversion can for analytical purposes be effected by either the enzyme, invertase, or by hydrochloric acid.

In its simplest form applicable to the ideal case, where nothing but the rotation of sucrose is altered, the Clerget formula is

$$\text{Percentage of } S=\frac{(P-P')}{C+ac-b(t-20)},$$

in which P and P' are the direct and invert polarizations, respectively, of the normal solution; C, the basic value of the Clerget divisor at 20° C; ac, the change in the value of the divisor with concentration of substance; and b, its change for each degree rise in temperature.

The Clerget formula is frequently applied in the above form without assurance that the fundamental condition is fulfilled, namely, that the rotations of all substances except sucrose remain unaltered in the two polarizations. In general, it is true that for samples containing high percentages of sucrose and small quantities of invert sugar the method yields reliable results and that for low-grade products it yields results which are sometimes sufficiently accurate for the purposes at hand.

Of the two commonly employed hydrolytic agents, invertase is the superior because of its highly selective action on the sucrose group and because it is without effect on the rotations of other substances occurring as impurities in sugar samples. Its disadvantages are its relatively high cost, the considerable labor required for its preparation, the uncertainty that the preparation has retained its activity, and, except under certain conditions, the long time required for the completion of the hydrolysis.

Hydrochloric acid, on the other hand, involves negligible expense and is capable of completing the hydrolysis in any desired period of time by merely regulating the temperature of reaction. However, it is not selective but hydrolyzes any glycosidic group. Moreover, it influences the rotatory power of invert sugar and many other impurities occurring in natural products.

2. ACID METHODS

(a) BASIC VALUES OF THE CLERGET DIVISOR

In devising the method, Clerget [1] in 1849 took 50 ml of a normal sucrose solution in a 50- to 55-ml flask, added 5 ml of "pure and fuming" hydrochloric acid, and after mixing, placed the flask in a water bath so regulated that 10 minutes were required to raise the temperature of the solution to 68° C. Upon attaining this temperature the flask was removed, cooled rapidly to 20°C, and the solution polarized.

The invert reading was multiplied by 11/10. The percentage of sucrose was calculated by the formula

$$S=\frac{100D}{144-\frac{t}{2}},$$

in which D is the algebraic difference between the two corrected polarizations and t is the centigrade temperature.

Browne [2] modified the Clerget method by allowing the solution to invert overnight at room temperature and making it to a volume of 55 ml at the completion of the inversion. It was pointed out that as the result of three factors a contraction in volume of about one-third of a milliliter occurred in the original method. The diminution in volume is caused, first, by the contraction which all sucrose solutions undergo during inversion and which for 13 g of sucrose in 55 ml is about 0.25 ml; second, the elevation of temperature caused by dilution of 5 ml of concentrated hydrochloric acid; and third, by the evaporation of water during the inversion. The advantage claimed by the author is that the invert solution, being but slightly diluted, can be observed with practically the same precision as the solution for direct polarization and with no great multiplication of errors, as is the case in methods in which the invert solution is more highly diluted. This advantage is lost, however, if the invert solution in the alternative methods is observed in a 400-mm column.

Browne found the percentage of sucrose to be expressed by the formula

$$S=\frac{100D}{144.9-\frac{t}{2}-0.01(144.9-\frac{t}{2}-D)},$$

in which the parenthetical term multiplied by 0.01 in the denominator is the correction of the divisor for concentration of sugar. If the concentration of sucrose is diminished from 26 to 25 g, the parenthetical term becomes roughly 5.19 and the concentration coefficient 0.052 for 1 g of sucrose. This value is considerably lower than the prevailing value 0.0676, and quite at variance with the revised value, 0.0794, of Jackson and McDonald discussed in a later paragraph.

Jackson and Gillis [3] showed that under the conditions prescribed by Browne inversion is complete in 8 minutes at 60° C.

In 1888 Herzfeld [4] devised the modification of the Clerget method which has remained in use to the present day. He observed the direct polarization in the usual manner, employing the normal weight of sucrose. He then took the half-normal weight (13 g) in 75 ml of solution, added 5 ml of hydrochloric acid (38 percent or 1.188 specific gravity), and warmed the solution to 67° to 70° C in from 2 to 3 minutes. The solution having attained the prescribed temperature, he kept it as near 69° C as possible for 5 minutes, when it was quickly cooled, made to a volume of 100 ml at 20° C, and polarized at the same temperature. Being that of a half-normal solution, the reading was multiplied by 2. Under these conditions he found the Clerget formula to be

$$S=\frac{100D}{142.66-0.5t}.$$

The basic value of the Clerget divisor in the above formula, 142.66, is defined as the algebraic difference between the rotation of the normal pure sucrose solution at 20° C (i. e., +100) and twice the rotation of 13 g of inverted sucrose in 100 ml at 20° C, corrected to 0° C by the term $+0.5t$. The actually measured value, free from the uncertainty of the value of the temperature coefficient, is 132.66 at 20° C.

The basic value of the divisor has been the subject of numerous investigations with different results. Herzfeld, in his original publication, adopted the value 132.66 at 20° C, but apparently the actual measurement was made by Dammüller [5]. Later investigators have invariably obtained higher values: Walker [6], 132.78; Tolman [7], 132.88; and Steuerwald [8], 133.05. Jackson and Gillis computed that by the Herzfeld procedure the destruction of invert sugar caused a lowering of the rotation by 0.15 to 0.20° S, which, deducted from their recalculated value, 133.18, left a resultant rotation of −33.03 to −32.98.

In 1920 Jackson and Gillis [3] published the results of a careful series of measurements in which they inverted sucrose solutions at 60° C instead of 70° C in order to avoid the destruction of invert sugar. They made their measurements at a somewhat higher concentration than the half-normal solution in order to utilize such standard quartz plates as were available, thus eliminating the errors of graduation of the saccharimeter scale. They were consequently obliged to correct their observed rotations for the higher concentration of sugar, using for this purpose the then prevailing value 0.0676 per g departure from 13 g of sucrose per 100 ml. Recent experiments have shown that this coefficient is considerably too low and that a recalculation of the Jackson and Gillis value for the rotation of the half-normal weight is necessary. Thus their originally announced value, −33.25, now becomes −33.18 at 20° C.

Subsequent to the publication of the Jackson and Gillis measurements, but previous to the appearance of the German translation of the same article [9], Herzfeld published a posthumous work of Schrefeld [10], whose experiments were made in 1910 to 1912. Schrefeld dissolved the half-normal weight of sucrose in 75 ml of water and added 5 ml of concentrated hydrochloric acid (sp gr 1.19). Inserting a thermometer in the sugar solution, he immersed the flask in a water bath having a temperature of 70° C, and agitated it until in 2½ to 2¾ minutes the solution had reached a temperature of 67° C. From this moment he allowed it to remain in the bath for exactly 5 minutes, during which time the temperature gradually rose to 69.5° C. The flask was removed and cooled rapidly to 20.0° C and the solution made up to 100 ml. Polarization measurements were made at 20° C. As a mean of seven concordant polarizations, Schrefeld found the rotation of the half-normal solution multiplied by 2 to be −33.00. This value has not been officially adopted by the International Commission for Uniform Methods of Sugar Analysis but has been widely used and has been verified by Browne. Zerban and coworkers under similar conditions found −32.97; Spengler, Zablinsky, and Wolf [11], −33.02; and Jackson and McDonald, −32.99. Thus the basic value, 133.00 at 20° C, for inversion under the Schrefeld conditions must be considered a well-established constant. It has been adopted officially by the Association of Official Agricultural Chemists.

Jackson and McDonald have experimentally corroborated the recalculated value −33.18 of Jackson and Gillis and have extended their measurements to include values obtained after inversion at several other temperatures. The Arrhenius formula, 37, evaluated by Jackson and Gillis, and discussed further on page 133 permits a calculation of the velocity constant of inversion at any desired temperature in the presence of 0.7925 *N* hydrochloric acid. With the aid of this equation, Jackson and McDonald [15] calculated the time required for 99.99-percent hydrolysis at 49° and 35° C, respectively, and measured the rotation of the half-normal solution. They found the value −33.25 for both temperatures.

Many analysts advocate inversion at room temperature as a safe means of avoiding decomposition of invert sugar. Formula 37 enables us to calculate the velocities of inversion and times required for 99.99-percent inversion at the temperatures which may be expected in uncontrolled laboratories. These periods of time vary considerably with small changes of temperature, as is shown in table 10. While the velocities of many reactions double themselves with a rise of 10 degrees in temperature, the velocity of inversion of cane sugar increases more than fourfold between 20° and 30° C. Thus room-temperature inversion is safe only if such variations of temperature as inevitably occur are known to the analyst and are considered in calculating the time required for complete hydrolysis. It appears from table 10 that 24 hours is insufficient for hydrolysis at 20° C, that 16 or 17 hours for overnight inversion at 30° C is excessive, and that serious decomposition of invert sugar can result. Evidently room-temperature inversion must be carried out with considerable discretion.

TABLE 10.—*Time required for inversion of sucrose at room temperature by 0.7925 N hydrochloric acid*

Temperature	Velocity[1] constant	Time for 99.99-percent inversion	Temperature	Velocity[1] constant	Time for 99.99-percent inversion	Temperature	Velocity[1] constant	Time for 99.99-percent inversion
°C		*Hours*	*°C*		*Hours*	*°C*		*Hours*
18	0.001590	41.9	24	0.003941	16.9	30	0.009421	7.08
20	.002161	30.8	26	.005290	12.6	32	.012502	5.33
22	.002924	22.8	28	.007073	9.4			

[1] Common logarithms and minutes.

For room-temperature inversion the value of the negative constituent of the Clerget divisor adopted by the Association of Official Agricultural Chemists is −33.20. Jackson and McDonald [15] have measured this constant with care by inverting the half-normal weight of sucrose in a thermostat which maintained a constant temperature within a few hundredths of a degree. The times of inversion were calculated by formula 37 for temperatures varying from 20° to 25° C. The mean value found for the rotation of the half-normal solution was −33.29.

In recapitulation, table 11 shows the values of twice the rotation of the inverted half-normal solution. All of these measurements except the first one at 70° C were made with care to avoid the destruction of invert sugar after the completion of the inversion. Jackson and Gillis showed that when sucrose is inverted by the Herzfeld method

in a bath at 70° C decomposition of invert sugar ensues as a result of too drastic conditions. Jackson and McDonald [15] have carried out the inversion in a 70° bath but have shortened the final period of heating from the prescribed 5 minutes to 3, 2, and 1 minute, respectively. In these measurements the value —33.00 for 5 minutes rose to a maximum of —33.08 at the 2-minute period. With this value included, all of the values in table 11 except the first represent twice the rotation of the inverted half-normal solution, the destruction of invert sugar after the completion of the inversion being avoided. It is evident that the rotation is definitely a function of temperature and that invert sugar is attacked by acid during the course of the inversion. Conceivably furanoid fructose, which has a transitory existence, is attacked by the acid, and increasingly so as the temperature rises.

TABLE 11.—*Variation of twice the rotation of the half-normal invert-sugar solution with varied conditions of inversion*

Temperature of inversion	Time	Rotation	Temperature of inversion	Time	Rotation
°C		*°S*	*°C*		*°S*
67 to 69	5 min	−33.00	49	38 min	−33.25
67 to 69	2 min	−33.08	35	205 min	−33.25
60	9.5 min	−33.18	25	17.2 hr	−33.29

The data in table 11 illustrate the importance of specifying the time and temperature of inversion for the standard values of the divisor and of adhering closely to the specifications in carrying out the analysis. For practical purposes there are three temperatures which require consideration. Room temperature is quite suitable if the precautions stated above are observed. For more rapid work the inversion can be effected in a bath regulated at either 60° or 70° C. At 70° there is a destruction of about 1 percent of invert sugar, and the analysis is incorrect unless such destruction occurs. It is quite possible to reproduce the value, —33.00, with relatively pure sugars, but the question arises whether in crude substances, which are heavily charged with inorganic salts of weak acids, the acid retains its activity. If by buffer action the activity of the acid is diminished, it is possible that the 1 percent of invert sugar is not destroyed and an error in the analysis would result, since the basic value of the divisor to be used at 70° requires that such decomposition occur. The same statements are of course true of the 60° inversion, but here only one-third of 1 percent of invert sugar must be destroyed. Moreover, such destruction occurs unavoidably during the process of inversion and not both during and after the inversion, as is the case at 70°.

These considerations make it appear that the 60° inversion advocated by Jackson and Gillis is preferable to that at 70°, but further experiments are required before a final decision can be made. It is true that at 60° many final molasses are not completely inverted in the specified period of time. Such samples would require either a prolonged time of inversion at 60° or an elevation of the temperature to 70°, and the value of the divisor under these altered conditions requires determination.

Until much additional work is done it appears advisable to employ alternatively three inversion temperatures, namely 70°, 60°, and that of the laboratory, and to use for each temperature the proper basic value of the divisor. Detailed methods are given on page 152.

Walker [12] has devised a method of inversion which has the advantage of requiring a minimum of attention. In this method 75 ml of the solution used for the direct polarization is transferred to a 100-ml flask and heated in a water bath to 65° C. The flask is removed from the bath, and to the solution is added 10 ml of HCl (d_4^{20} 1.1029). The solution is allowed to cool spontaneously in the air for 15 minutes or as much longer as may be convenient, made to volume, and polarized in the usual manner. The advantage claimed in addition to its convenience is that the maximum temperature coincides with the minimum quantity of invert sugar, and thus the destruction of levulose is diminished. Walker did not determine the basic value of the divisor, but Jackson and Gillis in a limited number of experiments found it in agreement with the value obtained by inversion at 60° C. It is, therefore, tentatively assigned a value of 133.18.

Low-grade products which were clarified by basic lead acetate suffered decomposition of reducing sugar during the period of heating as a result of the excess basic lead in the filtrate. Walker therefore advised, in these instances, the addition of 1 or 2 ml of acid to bring the solution to neutrality or slight acidity.

(b) VELOCITY OF INVERSION OF SUCROSE

The hydrolysis of sucrose, when catalyzed in dilute aqueous solution by acids, follows the unimolecular reaction formula

$$k=\frac{1}{t}\ln\frac{R_0-R_\infty}{R_t-R_\infty},$$

in which R_0 and R_∞ are, respectively, the initial and final rotations, and R_t is the rotation at the time t. Under any one set of conditions, k is constant during the course of the reaction but varies somewhat with the concentration of sugar and directly with the activity of the acid. An inspection of the chemical equation shows that two molecular species are involved in the hydrolysis, namely sugar and water. The amount of water which disappears is, however, in dilute solution quite insignificant in comparison with the amount of water present in the solution, and it is for the reason that the concentration of water remains practically constant that the unimolecular formula applies. That the reaction is of second order becomes evident if reaction velocities of different concentrations of sugar are compared. Thus Jackson and Gillis found the velocity constant 0.002161 for 19.5 g in 100 ml of solution at 20° C, while Jackson and McDonald found, under the same conditions of temperature and volume concentration of acid, a constant of 0.003355 for 83.3 g in 100 ml. This large difference of 50 percent is probably due to increased activity of the hydrochloric acid as well as to the increased concentration of sucrose.

Jackson and Gillis [3] measured the velocities of hydrolysis of sucrose in the presence of 0.01, 0.10, and 0.7925 N hydrochloric acid for a concentration of 13 g of sucrose in 80 ml of solution, over a wide range of temperatures.

Arrhenius [13] proposed the hypothesis that some molecules in a reacting system contained sufficient energy to react, while some were inactive, and, if the system contained a constant amount of energy there would be an equilibrium between active and inactive molecules. Thus

$$k=\frac{[\text{active molecules}]}{[\text{inactive molecules}]}.$$

The displacement of the constant with temperature follows the van't Hoff equation

$$\frac{d \log k}{dt}=\frac{Q}{RT^2},$$

in which Q is the energy of activation. If Q is constant over a wide range of temperatures, this equation can be integrated to the form

$$k_{T_2}=k_{T_1}e^{\frac{Q}{R}\left(\frac{T_2-T_1}{T_2T_1}\right)}, \tag{37}$$

in which T represents absolute temperature, and R is the gas constant. Jackson and Gillis applied this formula to their velocity-constant measurements with satisfactory agreement.

The data are computed to a usable form in table 12. These data are reproduced to serve as a guide for general use. They are applicable to a concentration of 13 g of sucrose in 80 ml and will deviate slightly for different concentrations of sugar.

TABLE 12.—*Time required at various temperatures for 99.99-percent inversion in the presence of 0.01, 0.1, and 0.7925 N hydrochloric acid as catalyzer*

Temperature	0.01 *N* HCl		0.1 *N* HCl		0.7925 *N* HCl	
	Velocity constant	Time for 99.99-percent inversion	Velocity constant	Time for 99.99-percent inversion	Velocity constant	Time for 99.99-percent inversion
° *C.*		*Hours*				
20	0.00001899	3,511	0.0002032	328 hr.	0.002161	30.8 hr.
25	.00003984	1,673	.0004264	156 hr.	.004569	14.6 hr.
30	.00008148	818	.0008737	76 hr.	.009427	7.1 hr.
35	.0001629	409	.001747	38.2 hr.	.01900	3.5 hr.
40	.0003186	209	.003453	19.3 hr.	.03785	106 min.
50	.001145	58	.01230	5.4 hr.	.1365	29.3 min.
60	.003806	17.5	.04151	1.6 hr.	.4606	8.7 min.
70	.01182	5.6	.1273	31.4 min.	1.447	2.76 min.
80	.03303	2.02	.3542	11.3 min.	--------	----------
90	.08982	0.74	--------	----------	--------	----------

(c) INFLUENCE OF CONCENTRATION OF SUGAR ON THE CLERGET DIVISOR

The specific rotations of both dextrose and levulose vary with the concentration of sugar, and that of invert sugar likewise varies with concentration, as is shown by the Gubbe [14] equation

$$[\alpha]_D^{20}=-19.447-0.06068p+0.000221p^2,$$

in which p is the percentage of invert sugar. Thus the basic values of the Clerget divisor discussed above are valid only for a concentration of 13 g of inverted sucrose.

Herzfeld applied to the basic value of the divisor the correction $0.0676\ (m-13)$, in which m is the weight of inverted sucrose in 100 ml

of the solution taken for the invert polarization. This value of the coefficient has remained in general use to the present day. Steuerwald found a slightly higher value, 0.0717. Herles found 0.067 and Sazavsky 0.0677.

Jackson and McDonald [15] have recently measured this coefficient by observing the polarization of a series of solutions prepared by dilution of an invert-sugar solution over a wide range of concentrations. By this procedure assurance was had that all variables such as those arising from the inversion reaction itself were eliminated, the only variable being that caused by dilution. Two series of measurements were made. In one series each solution contained 10 ml of 6.34 N hydrochloric acid in 100 ml, the condition which prevails in the acid Clerget method; in the other series no substance other than dextrose and levulose was present, the condition of the enzymotic method of analysis. The results are given in table 13. The respective coefficients are shown in the following formulas:

$$(0.634\ N\ \mathrm{HCl})\ P' = -(32.265 + 0.07935S)$$

$$(\text{Pure water solution})\ P' = -(30.994 + 0.08241S)$$

in which P' is the rotation calculated to 26 g of sucrose, and S is the weight of sucrose in 100 ml of solution. The relation proved to be linear between 2 and 26 g of sucrose.

TABLE 13.—*Measurement of the concentration coefficient of invert sugar*

10 ml of 6.34 N HCl $P' = -(32.265 + 0.07935°\ S)$			Synthetic invert sugar, $P' = -(30.994 + 0.08241°\ S)$		
Weight of sucrose	$-P'$, found	$-P'$, calculated	Weight of sucrose	$-P'$, found	$-P'$, calculated
g	° *S*	° *S*	*g*	° *S*	° *S*
26.000	34.33	34.33	25.6001	33.11	33.10
23.6201	34.13	34.14	23.2542	32.91	32.91
20.7796	33.93	33.91	20.4571	32.66	32.68
18.1639	33.68	33.70	17.8814	32.47	32.47
15.5841	33.51	33.50	15.3376	32.25	32.26
12.9891	33.29	33.29	12.7940	32.08	32.05
10.6115	33.13	33.11	10.1919	31.85	32.84
7.7942	32.84	33.89	7.6688	31.61	31.63
5.1782	32.71	33.68	---------	---------	---------

(d) EFFECT OF VARYING TEMPERATURE ON THE CLERGET DIVISOR

The specific rotation of levulose varies considerably with the temperature of observation, while that of dextrose is very nearly independent of temperature. The specific rotation of invert sugar, and consequently the negative constituent of the Clerget divisor, are therefore functions of temperature. Clerget found that the divisor diminished 0.5° S for each degree increase of temperature above 20° C, and applied the correction $-0.5t$ to his value 144.0, in which t is the centigrade temperature and 144.0 is the divisor extrapolated to 0° C. This does not imply that the value 144.0 is actually valid at 0°; it rather means that for relatively small deviations from 20° C, the correction is valid. If, as Zerban suggests, the basic value is defined as the reading at 20° C, the temperature correction becomes $-0.5\ (t-20)$. This value of the temperature correction has remained in general use to the present day. Tuchschmidt [16] in 1870 found

the value to be $-0.50578t$, but it is questionable whether the instruments available at that early date were capable of the precision required for so accurate a measure of the coefficient.

Zerban calculated from Vosburgh's observations that the coefficient for the half-normal (German) weight of sucrose would be -0.478 and for the quarter-normal weight, -0.466. Gillet [17] reported a value of -0.49 for the half-normal solution. Zerban states that the value -0.50 for final cane molasses at quarter-normal concentrations is considerably too high.

It is evident that considerable uncertainty attaches to the value of the temperature coefficient and that new careful measurements are urgently required.

The foregoing coefficients apply solely to the polarization of the inverted solution. Sucrose also has a definite, although small, temperature coefficient. The normal solution diminishes 0.03° S per degree increase of temperature, so that the negative temperature coefficients given above are to be increased to a higher negative value by 0.03° S when applied to the whole Clerget divisor. Pending further accurate measurements and general agreement, it appears necessary to use 0.53 for the temperature coefficient except in special instances where a different value is known to apply accurately.

In applying the Clerget divisor and its temperature coefficient to actual analyses, it is assumed that the solutions are made to volume and polarized at the same temperature, the saccharimeter wedges likewise being at this temperature. Zerban recommends that these readings be made at exactly 20° C in view of the uncertainty of the temperature coefficients. Evidently this difficult requirement can be met only by laboratories that have complete temperature control. It is urgent therefore that the temperature coefficients not only of the pure sugars, but also of the commonly occurring crude mixtures, be determined.

It frequently occurs that the two polarizations differ slightly from each other in the temperature of observation. In such a case it is preferable to calculate the results from the temperature of the invert polarization alone and, whenever possible, to correct the direct polarization and the quartz wedges to this temperature. If the temperature of the wedges differs from that of the solution under observation, the reading can be corrected to the temperature of either solution by applying the temperature coefficient of quartz, namely 0.000148 per degree temperature per degree sugar. Since the effect of the coefficient is to lower the reading of the scale with increase of temperature, the apparent polarization is lower than it should be. Thus if a solution polarizes 100° S and the wedges are 1 degree centigrade higher than the solution, the reading must be increased by 0.015. Obviously these corrections need be made only for high polarizations and considerable differences in temperature.

If the solution for direct polarization is free from invert sugar, as is the case with beet products, and if made to volume and polarized at a temperature different from that of the invert polarization, it can be corrected to the temperature of the latter by

$$P_t = P_t' + 0.0003P(t' - t),$$

in which t and t' are the temperatures of the invert and direct polarizations, respectively.

If, finally, the solutions for direct and invert polarizations were made to volume at the same temperature but polarized at different temperatures, the direct polarization (if free from invert sugar) can be corrected to the temperature of the invert polarization by

$$P_t = P_{t'} + 0.00061P(t' - t),$$

in which the coefficient includes the changes arising from the change of rotary power of sucrose and the expansion of the solution.

(e) EFFECT OF HYDROCHLORIC ACID

Many dissolved substances affect the rotation of invert sugar, the greater number elevating it to a higher negative rotation but some altering it in a positive direction. Hydrochloric acid is most commonly used as the inverting agent, and its effect has been shown to increase the negative rotation to a higher negative value. Jackson and Gillis studied this effect quantitatively and found that the negative rotation was enhanced as the concentration of acid was increased, the relation being precisely linear up to 1.3 N hydrochloric acid and approximately so up to 2.5 N. They confined their measurements to a single concentration of invert sugar, namely that formed by the inversion of 13 g of sucrose in 100 ml of solution. In their formula, R and R_0 represent the rotation at 20°C of 13 g of inverted sucrose multiplied by 2, m the grams of hydrochloric acid, and N the normality of the acidified solution.

$$R = R_0 - 0.5407m = R_0 - 1.972N. \tag{38}$$

If we select for a stock hydrochloric acid one having a normality of 6.34 (d_4^{20} 1.1029),

$$R = R_0 - 0.125v, \tag{39}$$

in which v is the number of milliliters of 6.34 N acid in 100 ml of the solution polarized.

It is evident from these equations that the concentration of acid should be carefully regulated. Instead of the 5 ml of concentrated acid previously used, Jackson and Gillis recommended dilution of strong acid to 6.34 N or d_4^{20} 1.1029. This constitutes a 1:1 dilution if the original concentrated acid contained exactly 38.8 percent of hydrochloric acid. As this is seldom the case, it is preferable to adjust the diluted acid to the concentration specified. This specification has been adopted by the Association of Official Agricultural Chemists [18]. Ten milliliters are used for inversion.

If in eq 39 the correction term which, evaluated for 10 ml of 6.34 N hydrochloric acid, becomes −1.25°, is applied, and if the experimentally determined values of R given in table 14 are then substituted, the equations can be solved for R_0, the rotation of invert sugar in the absence of acid. If no decomposition of invert sugar during the inversion reaction occurred, R_0 would equal the rotation of pure invert sugar, or in other words, the Clerget divisor by the invertase method. For the acid inversion at 70° C, R_0 becomes −31.75; for 60° C, −31.93; for room temperature, −32.03; and for 4°C, −32.08. The accepted value for invert sugar by invertase inversion is −32.10. Evidently in all methods of acid inversion, decomposition of invert sugar occurs, but to a diminishing extent as the temperature of inversion is decreased.

(f) EFFECT OF VARIOUS REAGENTS ON THE ROTATION OF INVERT SUGAR

An effect on the rotation of invert sugar similar to that of hydrochloric acid is produced by neutral salts. It is thus not because of its acidity that hydrochloric acid enhances the negative rotation of invert sugar, but rather because it, like many salts listed below, is a dissolved substance which, conceivably on account of its high degree of solvation, produces an effect similar to an increase in concentration.

Jackson and Gillis [3] studied systematically the effect of various reagents on the rotation of invert sugar. They derived the formulas given in table 14, in which R is twice the rotation in saccharimeter degrees of the half-normal solution, and m the weight in grams per 100 ml of the substance (anhydrous) whose effect is measured. Further but less detailed measurements are given in table 15.

TABLE 14.—*Effect of salts on the rotation of invert sugar* [a]

Salt	R	Molecular depression	Equivalent depression
HCl	$R=-32.10-0.5407\ m$	19.71	19.71
$NaCl$	$R=-32.10-0.540\ m$	31.56	31.56
NH_4Cl	$R=-32.10-0.563\ m$	30.12	30.12
$CaCl_2$	$R=-32.10-0.710\ m$	78.80	39.90
$K_2C_2O_4$	$R=-32.10-0.510\ m$	84.77	42.39
H_3PO_4	$R=-32.10-0.0776\ m$		
$HC_2H_3O_2$	$R=-32.10+0.0823\ m$		

[a] In their original article, Jackson and Gillis used the value −32.00 for invert sugar in the absence of reagents. However, they determined merely the slope of the curves upon addition of reagents. The substitution of the correct value, −32.10, does not affect their measurement of the slope.

It will be recognized that the list of salts is far from comprehensive, but the data show clearly that relatively large variations in the rotatory power of invert sugar can arise as a result of the admixture of salts and furthermore that the anion produces unpredictable effects.

Under the column headed "molecular depression" is given the depression caused by 1 mole of dissolved substance, and under "equivalent depression" that caused by the salt calculated to valence 1. A very rough similarity in the equivalent depression caused by the sodium, potassium, and ammonium salts seems to occur, 1 molecular equivalent depressing the rotation by 25° to 40° S. Further reference will be made to this relation under a discussion of Saillard's modification of the Clerget method.

Attention should be directed to the well-known effect of basic lead acetate on the rotation of invert sugar. This is probably due to a chemical combination of the basic lead constituent with levulose and illustrates the necessity of acidifying the direct polarization of a crude substance which contains invert sugar and which has been defecated

TABLE 15.—*Influence of various reagents on the rotation of invert sugar*

Reagent	Change in rotation per gram in 100 ml	Equivalent depression	Reagent	Change in rotation per gram in 100 ml	Corresponding equivalent depression
	°*S*	°*S*		°*S*	°*S*
$Pb(C_2H_3O_2)_2yPbO$	+1.43		KCl	−0.486	38.6
$Pb(C_2H_3O_2)_2$	−0.020		$Na_2HPO_4 12H_2O$	−.161	28.8
NH_4NO_3	−.399	31.9	$NaC_2H_3O_2$	−.314	25.8

with basic lead. Acetic acid, and probably many other weak organic acids, change the rotation of invert sugar in a positive direction.

(g) ROTATION OF SUGAR MIXTURES AND THE EVALUATION OF m

It has been shown above that the rotatory power of pure invert sugar increases in a negative sense with increase in concentration, and that for the analysis of pure sucrose the Clerget divisor must be increased by the quantity 0.0794 ($m-13$), in which m is the number of grams of sucrose taken in the sample for the invert polarization. The question now arises as to what the value of m is if the original sample contains invert sugar, organic nonsugars, or inorganic salts in admixture with sucrose. In general, sugar-cane products contain all four of these constituents, while beet products usually contain all except invert sugar.

Consider first the analysis of a mixture of sucrose and invert sugar. The essential condition of the Clerget method is that the rotation of the invert sugar in the direct polarization be the same as in the invert polarization. Jackson and Gillis [3, 9] showed that a given quantity of invert sugar in the presence of sucrose had a slightly lower negative rotation than it would have if all of the sucrose were inverted. However, since its rotation approached constancy more closely if the concentration of total sugar were unaltered than if the relatively large effects of dilution were introduced, they recommended that both direct and invert polarizations have the same concentration of the sample. This expedient was admitted by the authors to be a first approximation "since the problem of the rotation of mixtures was too large a one for a complete solution at that time." If now the plausible assumption is made that the rotatory power of sucrose is unaltered by admixture with invert sugar, its change of rotation upon hydrolysis would be from the positive rotation of sucrose itself to the negative rotation of invert sugar at the concentration of total invert sugar, which is the sum of the invert sugar formed by hydrolysis and the invert sugar originally present. Since the variations in the Clerget divisor are caused only by the variations of the specific rotation of invert sugar with concentration, the quantity m should represent the grams of total sugar in 100 ml of solution rather than the grams of sucrose.[7]

Vosburgh [19] in a more general study measured the rotations of mixtures of sucrose, dextrose, and levulose and stated his results in an article which has been widely quoted and very frequently misquoted. Vosburgh summarized his conclusions as follows:

1. The specific rotations of glucose and fructose when mixed in equal proportions (invert sugar) are those which the sugars would have if each were present alone at a concentration equal to the total invert-sugar concentration.
2. In mixtures of glucose and sucrose the specific rotations of the two are those which the sugars would have if each were present alone at a concentration equal to the total sugar concentration.
3. The relationship is only approximate for mixtures of fructose and sucrose, in which case the rotation is a little smaller (or larger numerically if negative) than that calculated upon its assumption.

[7] This is a reversal of the recommendation of Jackson and Gillis, who substituted for m the grams of sucrose alone.

4. The polariscopic determination of the percentage of sucrose replaced by invert sugar gives slightly high results.

It should be noted that the statement in conclusion 1, which was confined to pure invert sugar and was not even applied to all dextrose-levulose mixtures, has frequently in subsequent literature been extended to apply not only to all sugar mixtures but to all sugar-nonsugar mixtures. Conclusion 4, which concerns the Clerget analysis specifically, implies that conclusion 1 does not apply exactly to sucrose-invert sugar mixtures, the deviation amounting to about 0.4 percent, an error quite appreciable in Clerget analysis. This conclusion is in harmony with the previously described experiment of Jackson and Gillis, although the precision of analysis by the invertase method and by the compensation methods described in later paragraphs is closer than 0.4 percent. It should be recognized that the expedients suggested in this paragraph are recommended as approximations and are subject to alteration as knowledge of the rotations of sugar mixtures advances.

Zerban [20] in an extensive study of the analyses of complex sugar mixtures showed that satisfactory agreement of calculated and determined values of sucrose was obtained if "in these calculations the divisor corresponding to the total sugar concentration, and not that for the sucrose concentration, is used." In other words, m represents the number of grams of total sugars taken for inversion and made up to 100 ml after inversion.

In a further study Zerban prepared samples simulating cane molasses by combining accurately known quantities of its constituents, and here he found it necessary to assign to m the total weight of dry substance taken for inversion.

(h) INFLUENCE OF REAGENTS ON THE ROTATION OF SUCROSE

Sugar sirups of commercial importance frequently contain appreciable quantities of inorganic salts. Cane and beet molasses are essentially sirups in which, by removal of sugar, the salts have accumulated to such an extent that no further crystallization of sugar is possible. The presence of salts causes an alteration of the rotatory power of sucrose and, therefore, not only is the direct polarization of plant juices rendered uncertain, but both the direct and invert polarizations of the Clerget method are affected and the analytical results are made uncertain unless the change in the direct is the same as in the invert polarization.

In general, dissolved inorganic salts diminish the rotatory power of sucrose. For a few salts, Jackson and Gillis measured this depression and found it linear with respect to concentrations of salt ranging between 0 and about 4 g in 100 ml. They established the relations shown in table 16.

TABLE 16.—*Effect of salts on the rotation of sucrose*

Salt	R	Molecular depression	Equivalent depression
$NaCl$	$R=100-0.265\ m$	15.5	15.5
NH_4Cl	$R=100-0.169\ m$	9.0	9.0
$CaCl_2$	$R=100-0.339\ m$	37.6	18.8
$K_2C_2O_4$	$R=100-0.234\ m$	38.9	19.4

In the early literature [21] efforts were made to find some regularity between the depression and the molecular weight of the salt, and indeed the "molecular depression," that is, the depression caused by 1 g multiplied by the molecular weight, approached constancy for a few closely related salts, such as the chlorides of barium, strontium, and calcium. But molecular depression failed of constancy if applied more generally. Evidently in the relations listed above no constant molecular depression can be observed.

The depression caused by a given quantity of salt is, in dilute solution, a constant percentage of the rotation of pure sucrose quite regardless of the concentration of the latter. Thus Jackson and Gillis [22] showed by their own measurements and by calculation of the careful measurements of Browne [23] that 3.392 g of ammonium chloride produced the same relative depression on the rotation of sucrose, even when the concentration of the latter was varied between 5 and 52 g in 100 ml. When all rotations were calculated to 26 g of sucrose, the depressions were found to be the constant quantity 0.56° S. Similarly, 2.315 g of sodium chloride in 100 ml of a sucrose solution caused depressions of rotation which, when calculated to 26 g of sucrose, amounted to 0.62° S, quite regardless of the concentration of sugar.

Brown [24] extended these studies to very low concentrations of sugar and various salts, expressing this relation by the formula

$$\text{Percentage of sugar} = P + KPM,$$

in which P is the polarization, M the weight in grams of the salt present in 100 ml of the solution polarized, and K a constant which is characteristic for each salt. The following values of K were found mainly by measurement in very dilute solution, and with inevitable multiplication of error:

Salt	*K*
$NaCl$	0.00246
K_2SO_4	.00199
$Na_2SO_4.10H_2O$	.00205
$Na_2HPO_4.12H_2O$	.00305

Brown thus agreed with Jackson and Gillis that the depressive effect of salt was the same relative fraction of the total polarization regardless of concentration. Hence the values of K can be determined at high concentrations where the errors are small and applied to the low concentrations of thin juice and other dilute sirups.

(i) METHODS OF COMPENSATION

The direct application of the Clerget method in unmodified form to low-grade cane and beet products frequently leads to the introduction of analytical errors which are due to the effects of impurities in such samples. Cane products usually contain, in addition to sucrose, invert sugar which in the case of molasses may amount to 30 percent or more of the total sugar. It is necessary that the rotation of this invert sugar remain unaltered in both the direct and invert polarizations. Mention has already been made of the necessity of observing both polarizations in the same concentration of substance in order to avoid the change in rotation caused by dilution. An additional source of error is introduced in the acid methods of inversion as a result of the

fact that the invert sugar which is present as an impurity has its rotation increased negatively in the invert reading in the presence of the hydrochloric acid. Browne [25] has shown by applying the simple acid Clerget method to pure synthetic mixtures of invert sugar and sucrose that gross inaccuracies can be caused by the changed rotation of the added invert sugar in the two polarizations.

TABLE 17.—*Errors of analysis of sucrose caused by invert sugar*

Invert sugar	Sucrose		Invert sugar	Sucrose	
	Found	Taken		Found	Taken
g/100 ml	*Percent*	*Percent*	*g/100 ml*	*Percent*	*Percent*
1.10	96.18	96.15	8.21	38.99	38.46
2.74	77.10	76.92	9.86	19.82	19.23
5.48	58.14	57.69	----------	----------	----------

Jackson and Gillis sought to avoid this source of error by adding to the solution for direct polarization a neutral salt in such quantity that its effect on the invert sugar just equalled that of hydrochloric acid. The effects of added reagents on the rotation of invert sugar have been described on page 137. It was shown that 10 ml of 6.34 *N* hydrochloric acid in 100 ml increased negatively the rotation of the negative constituent of the divisor by 1.25° S. From the list of neutral salts it can be computed that 2.312 g of sodium chloride in 100 ml produces the same change of rotation. If, therefore, this weight of salt is added to the solution for direct polarization, the invert sugar present as an impurity will have the same rotatory power in both polarizations. But the addition of salt has now diminished the rotatory power of the normal sucrose solution from 100° to 99.38° S. The total change in rotation of sucrose is then from 99.38 to —33.18, and the Clerget divisor becomes 132.56 at 20° C. This is the basis of the Jackson and Gillis method IV described on page 155.

Nitrogenous substances consisting mainly of amino acids and their internally compensated salts occur in both beet and cane molasses. Many of these are optically active but possess one rotatory power in acid solution and quite a different one in neutral or alkaline solution. In order to compensate for this source of error Saillard [26] proposed that the invert solution be neutralized with sodium or potassium hydroxide. The method was elaborated in greater detail by Jackson and Gillis, who proposed that ammonia be used for neutralization because it had less destructive action on invert sugar than the more caustic alkalies. The neutralization of 10 ml of 6.34 *N* hydrochloric acid with ammonia produces 3.392 g of ammonium chloride; this causes an increased value of the negative constituent of the Clerget divisor, making it —33.84. This method of compensation was designed for beet products which were free from invert sugar. The basic value of the Clerget divisor becomes 133.84 for inversion at 60° C, or 133.94 for room-temperature inversion. This was designated Jackson and Gillis method III.

Many samples of sugar products contain both invert sugar and amino acids. Jackson and Gillis in method II sought to compensate for the altered rotation of these substances by neutralizing the solution

323414°—42——11

for invert polarization with ammonia and adding 3.392 g of ammonium chloride to the solution for direct polarization. This diminishes the rotation of sucrose from 100° to 99.43° S. The basic value of the divisor according to this method is 133.27.

Method III has had such limited use that it will not be described in the present Circular. While it is capable of eliminating the errors which otherwise would be introduced by the altered rotations of aminoacids, it still serves no useful purpose, because quite invariably products which contain aminoacids also contain raffinose. Such products, therefore, contain three unknown quantities and cannot be analyzed accurately by processes which yield but two equations. The method, however, has been utilized by Osborn and Zisch, whose procedure is described in a later paragraph (p. 160).

Saillard [27] has emphasized the fact that molasses contains sodium and potassium salts of organic and inorganic acids which diminish the rotation of sucrose and increase the levorotation of invert sugar. These two effects are incompletely compensated, the effect on invert sugar being the greater. His proposed remedy is to determine the ash content of each sample, and in a control test to determine the Clerget divisor by adding to pure sucrose and to the invert-sugar solution sodium or potassium chloride in amount equivalent to the ash in the sample. Thus for beet molasses no less than four polarizations and an ash analysis are required for a single Clerget test. Saillard's proposal has not been put into extensive practice, primarily because of the prohibitive labor involved. Moreover, the procedure rests on a questionable basis, because the assumption is made that sodium and potassium chlorides produce the same effects as the alkali salts of all other acids, regardless of the nature of the anion. In other words, Saillard unwittingly assumes the constancy of "molecular depression," which numerous previous experiments had shown was lacking. Nevertheless, it is quite possible that Saillard's procedure diminishes the error caused by alkali salts in the sample, and it would be desirable to investigate the effects upon the rotations of sucrose and invert sugar of the particular alkali salts which are known to occur in molasses. The special determination of the divisor for each test recommended by Saillard appears to be an unnecessary complication, for we have complete equations for the effects of sodium chloride upon sucrose and invert sugar and of potassium chloride upon invert sugar. If the procedure should prove of value, these equations could be solved for any desired concentration of salt.

Zerban and Gamble [28] have studied the question by preparing and analyzing known solutions of sucrose mixed with low-purity products of high ash content and observed no noticeable effect on the Clerget divisor, provided the divisor was based on the dry-substance concentration. (See conclusion 10, p. 145).

The ingenious suggestion has been made by R. J. Brown, who pointed out that the data of Jackson and Gillis showed that the effect of a given quantity of salt was approximately twice as great on invert sugar as on sucrose, and that in the absence of invert sugar in the sample, if the concentration of salt in the invert polarization is half as great as in the direct, the effect is completely compensated in the two polarizations. It is then merely necessary to use the normal weight for the direct polarization and the half-normal weight for the invert polarization.

(j) CREYDT RAFFINOSE FORMULA

Creydt [29] has shown that, in the absence of other optically active substances, sucrose and raffinose can be estimated by the Clerget method. This estimation depends upon the fact that for the solution of two unknown quantities two equations are sufficient. One of these equations states that the direct polarization is the sum of the rotations of the two constituents, and the other states that the invert polarization is the sum of the rotations of the products of hydrolysis.

Assume that the analysis is conducted at 20° C and that the normal weight of the sample is contained in 100 ml. Let the sample contain S percent of sucrose and R percent of anhydrous raffinose. Since the specific rotation of anhydrous raffinose is +123.2, while that of sucrose is +66.5, the raffinose in the mixture will have 1.852 times as great a rotatory power as an equal weight of sucrose. The direct polarization then will be

$$P=S+1.852R. \tag{40}$$

Let the invert solution contain 13 g of sample and the reading in the presence of 0.634 N hydrochloric acid be multiplied by 2. Raffinose, upon inversion, yields a mixture of levulose and melibiose, the resultant rotation of which was, according to early measurements, 0.5124 times the rotation of the unhydrolyzed raffinose. Browne and Gamble [30], revising this ratio, found the value 0.514. Osborn and Zisch [31] found a slightly lower value, but nevertheless accepted and used the value 0.514. The structure of the Creydt formula is such that small variations in the raffinose inversion factor have little effect upon the calculated sucrose or raffinose percentages. The invert polarization of the raffinose constituent is then $0.514\times1.852R=0.952R$. The invert reading of inverted sucrose varies slightly with the method of inversion. If we accept the Schrefeld method, the basic value of the negative constituent of the Clerget divisor is −33.00, while if we employ the Jackson and Gillis method of inversion at 60° C, the divisor is −33.18; if the method of overnight room-temperature inversion is employed, the value becomes −33.29. It is therefore necessary to derive three slightly different Creydt formulas.

If we assume that the basic value of the divisor is 133.00 at 20° C,

$$P'=-0.3300S+0.952R, \tag{41}$$

whence, upon elimination of R from eq 40 and 41

$$S=\frac{0.5140P-P'}{0.8440} \text{ at } 20°C, \tag{42}$$

and

$$R=\frac{P-S}{1.852}. \tag{43}$$

The derivation is quite similar when the other values of the divisor are used, the resulting formulas differing only in the values of the denominator, as appears in columns b and c in table 77, p. 563. These formulas are valid only at 20° C and for 13 g of dry substance taken for the invert polarization.

The direct and invert polarizations of sucrose vary with temperature,

$$P=S(1-0.0003(t-20))=S(1.006-0.0003t)$$
$$P'=S(-0.3300+0.005(t-20))=S(-0.4300+0.005t).$$

Browne and Gamble [30] have shown that the change of direct polarization of raffinose with temperature is very nearly the same as that of sucrose. The direct polarization of a mixture of sucrose and raffinose is then

$$P=S(1.006-0.0003t)+1.852R(1.006-0.0003t). \tag{44}$$

The accepted value of the temperature correction of the negative constituent of the Clerget divisor is $+0.5t$. Browne and Gamble have measured the change of polarization of invert raffinose with temperature, and have found that a solution of raffinose having a direct polarization of $+1.00$ would have an invert polarization of $+0.478+0.0018t$. The invert polarization of a mixture of sucrose and raffinose would then be

$$P'=S(-0.4300+0.005t)+1.852R(0.478+0.0018t). \tag{45}$$

This equation is strictly valid only for 13 g of dry substance taken for inversion, and a further correction of $-0.000794\ (m-13)$ must be applied to the parenthetical coefficient of S.

Simultaneous solution of eq. 44 and 45 and the introduction of the concentration correction yield

$$S=\frac{P(0.478+0.0018t)-P'(1.006-0.0003t)}{(1.006-0.0003t)[0.908-0.0032t+0.000794(m-13)]} \tag{46}$$

$$R=\frac{P-S}{1.852}. \tag{47}$$

Equation 46 is cumbersome to handle in ordinary analytical work. In order to facilitate its application, the respective coefficients have been computed and assembled in table 77, p. 563. Equation 46 may be expressed in the form

$$S=\frac{aP-bP'}{bc+0.000794(m-13)}, \tag{48}$$

and the coefficients a, b, c, and bc may be calculated for various temperatures. The term "c" is valid only for 13 g of dry substance, and for any variation of concentration the correction $+0.000794\ (m-13)$ as determined by Jackson and McDonald [15], or $+0.000676$ as used by Herzfeld, must be applied to the denominator.

The Creydt formula, as is shown by its derivation, is valid only in the absence of other optically active substances than sucrose and raffinose. Beet products contain, in addition to these sugars, optically active nitrogenous substances, the presence of which vitiates the formula with respect to precision. It is, however, extensively used and the errors of analysis are tolerated. For strict accuracy the double-enzyme method or, in certain localities, the double-acid method of Osborn and Zisch [31] is required.

(k) WORK OF ZERBAN AND COLLABORATORS

Zerban and Gamble [32] have summarized the work of The New York Sugar Trade Laboratory in a series of articles [33] and have applied the principles to a study of the analysis of crude products. The solutions previously analyzed contained known amounts of sucrose in mixture with invert sugar; reversion products of invert sugar; the amino compounds asparagine and aspartic acid, which are the principal substances of this nature found in cane products [34]; and salts.

The four inversion methods employed were: (a) The official invertase method of the Association of Official Agricultural Chemists [18] p. 470, (b) Jackson and Gillis method II [3, p. 184], (c) Jackson and Gillis method IV [3, p. 187]; and (d) Schrefeld's modification of the Herzfeld plain acid method [10]. The inversions were carried out mostly at room temperature, but in some of the work higher temperatures were employed; 55° C in method (a), 60° C in methods (b) and (c), and 67° to 69.5° C in method (d).

The results of these investigations may be summarized briefly as follows:

1. The solution used for the direct polarization must have the same dry-substance concentration as the solution used for inversion.
2. The Clerget divisor must be based on the dry-substance concentration and not on the sucrose concentration or on the invert reading alone.
3. It is preferable whenever possible to carry out the inversions at room temperature, because at high temperatures slight variations in the time used may have an appreciable effect on such reactions as the destruction of invert sugar in the presence of strong acid, on the hydrolysis of inversion products, and on the interaction between invert sugar and amino compounds.
4. The invertase method is the only one of the four methods compared which may be depended upon to give reliable sucrose results.
5. The sucrose result by Jackson and Gillis method II is increased by reversion products hydrolyzed under the conditions of the analysis.
6. The sucrose result by Jackson and Gillis method IV is increased by the hydrolysis of the reversion products in the same way as in method II, but aspartic acid or asparagine lowers the sucrose result considerably.
7. Accordingly, the difference between the sucrose result by Jackson and Gillis method II and that by the invertase method gives a relative measure of the reversion products hydrolyzed by hydrochloric acid under the conditions of the analysis.
8. The difference between the sucrose result by Jackson and Gillis method II and that by method IV gives a relative measure of the amino compounds present.
9. The plain acid method may give any kind of result, high, low, or correct within the limits of error, depending on the relative proportions of levulose, reversion products, and amino compounds present.
10. In the case of mixtures of known amounts of sucrose with a practically sucrose-free low-purity product, containing 13.74 percent of ash on the basis of dry substance, the salts, as such, had no noticeable effect on the Clerget divisor for any of the four methods investigated, provided the divisor was based on the dry-substance concentration.

The four methods which had been applied to artificial mixtures containing known quantities of sucrose were then used in the analysis of various blackstraps and refinery sirups. The inversions were carried out at a temperature of 26° to 30° C, and the polariscopic readings were made at the standard temperature of 20° C. The results, which are averages of many analyses calculated in accordance with rules 1 and 2 given above, are shown in table 18.

TABLE 18.—*Comparsion of sucrose found by four Clerget methods*

Number of samples	Material	Invertase	Jackson and Gillis method II	Jackson and Gillis method IV	Plain acid method
		Percent	*Percent*	*Percent*	*Percent*
8	Filtered sirups	34.86	35.43	35.14	35.25
6	Refinery blackstraps	33.34	34.46	33.85	34.11
9	Raw-sugar blackstraps	33.65	----------	34.12	34.27

Without exception, Jackson and Gillis method II gave higher figures than either the invertase method or Jackson and Gillis method IV. This shows that all the samples contained reversion products as well as amino compounds. The quantity of the reversion products, expressed as sucrose, in the refinery blackstraps varies from 0.64 to 1.32 percent, averaging 1.12 percent; and the quantity of amino compounds from 0.40 to 0.89 percent, averaging 0.61 percent. In the filtered sirups there are found 0.10 to 1.03 percent, averaging 0.57 percent, of reversion products, and 0.11 to 0.66 percent, averaging 0.29 percent, of amino compounds, all again expressed as equivalent sucrose. Expressed as asparagine or aspartic acid, the content of amino compounds in blackstraps and refinery sirups is, according to data given by Ambler [35] and by Browne [36], very much higher, in the neighborhood of 2 to 2.5 percent.

Leaving out Jackson and Gillis method II, and comparing the results of the other three methods for all the three groups of products analyzed, it is found that the plain acid method gives the highest average results, 0.10, 0.26, and 0.15 percent, respectively, higher than Jackson and Gillis method IV. The average figures by this last-named method again exceed those of the invertase method by 0.28, 0.51, and 0.47 percent, respectively, owing to the differential effect of reversion products and of amino compounds.

The application of the results, previously obtained with artificial mixtures, to the analysis of actual cane products has thus shown that Jackson and Gillis methods II and IV, used in conjunction with the invertase method, give valuable indications with regard to the relative quantities of reversion products and of amino acids present in such products.

3. INVERTASE METHODS

(a) PREPARATION OF INVERTASE

The enzyme, invertase, which can be prepared simply and abundantly from yeast, hydrolyzes sucrose under suitable conditions to invert sugar. The invertase prepared from "top" or baker's yeast inverts sucrose to invert sugar and also hydrolyzes raffinose to a mixture of levulose and melibiose, while a similar preparation from

"bottom" or brewer's yeast contains also the enzyme, melibiase, and hence possesses the additional power to hydrolyze melibiose to a mixture of dextrose and galactose. It is thus possible, as Hudson and Harding showed [37], to devise analytical processes for the determination of sucrose and raffinose in their mixtures or in crude beet-sugar products which contain them.

The two stages of the hydrolysis may be expressed as follows:

I. Sucrose (invertase present)→ invert sugar.
   Raffinose (invertase present)→ levulose+melibiose.
II. Melibiose (melibiase present)→ galactose+dextrose.

Reynolds [38] has given detailed directions for the preparation, purification, and concentration of highly active invertase and melibiase solutions. For the preparation of invertase (free from melibiase), 10 pounds of baker's yeast are broken up and mixed with 5 liters of water. Two liters of toluene are added and the mixture is stirred at frequent intervals throughout the first 24 hours. The autolysis is allowed to continue for 7 days. The extract is then filtered by gravity on large fluted filters, yielding about 5 liters of filtrate. The residue is mixed with 2 liters of water and filtered. The two filtrates are combined and show usually an activity of $k=0.028$ (see p. 150) The 7 liters of filtrate are transferred to the ultrafilter, described below, concentrated to 1 liter, and washed with 1 liter of water. The concentrated extract is removed from the ultrafilter, diluted again to 7 liters, acidified with 14 ml of glacial acetic acid, and allowed to stand overnight. This produces the precipitation of flocculent material which is removed by slow filtration through paper. As soon as a sufficient quantity of solution has filtered, it is transferred to the ultrafilter and its concentration continued simultaneously with the filtration from the flocculent precipitate. The extract is concentrated to a volume of 800 ml. In an instance cited by Reynolds, the activity of one such preparation was $k=0.22$.

For the preparation of invertase-melibiase 2.5 gallons of beer yeast is filtered on a large Büchner funnel to remove the wort. About 5,500 g of compressed yeast containing about 23 percent of solids is obtained. This is placed in a jar and 3 liters of toluene added. In a few hours the yeast becomes liquid and autolysis is continued for 7 days, the liquid being agitated once or twice each day. The extract is filtered by gravity on large fluted filters, yielding in 48 hours about 3 liters of filtrate. The residue is mixed with 1,200 ml of water, allowed to stand overnight, and again filtered. The combined filtrates should have an approximate volume of 4,200 ml and an activity of $k=0.0818$. The crude extract is ultrafiltered to a volume of 600 to 700 ml and washed with 1 liter of water. It is then diluted to 4 liters, treated with 8 ml of glacial acetic acid, and allowed to stand overnight, filtration through fluted paper funnels being started the next morning. Ultrafiltration is started as soon as sufficient filtrate has accumulated and is continued until the volume has been reduced to about 600 ml, whereupon it is washed with 3 liters of distilled water. The final extract is, if necessary, filtered again through paper. Reynolds found in one instance an invertase activity of $k=0.554$ and a melibiase activity of $k=0.024$. During ultrafiltration the solution is stirred with a motor-driven stirrer; otherwise the enzyme is liable to concentrate and precipitate at the membrane. Water should flow

through the membrane at the rate of 500 ml per hour, but the enzyme solution filters much more slowly, from 25 to 100 ml per hour, depending to some extent upon the vacuum applied. A membrane once properly prepared can be used continually for months and maintains practically the same permeability. When not in use, it should be kept covered with water to which a preservative has been added, e. g., a 1 : 2000 solution of chinosol.

(1) Collodion Ultrafilter.—Dissolve 6 g of soluble (in alcohol and ether mixture) pyroxylin or nitrocellulose, such as Astoria's, in a mixture of 50 ml of absolute alcohol and 50 ml of absolute ether by first adding the alcohol to the cotton, allowing the mixture to stand in a stoppered flask for 10 minutes, adding the ether, and shaking. Allow the solution to stand overnight, pour about 100 ml into a 2,000-ml

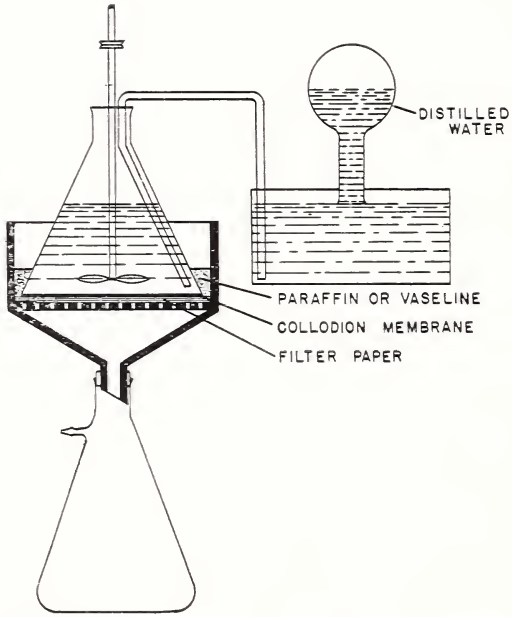


Figure 36.—*Ultra filter for purification of enzymes.*

cylinder, and coat the entire inside surface of the cylinder with the collodion. Drain, and dry for 10 minutes. Fill with water, let stand 10 to 15 minutes, pour out the water and remove the collodion sack. Test for leaks by filling with water. Slit open longitudinally and cut out a circular piece about 7 to 8 inches in diameter. Cut the bottom from a 2-liter bottle or Erlenmeyer flask and grind the edge smooth. Place it upon the still moist collodion disk, fold the edge of the disk up around the bottle, and cement it thereto with collodion that contains an increased percentage of ether. Place three or four thicknesses of wet filter paper in an 8-inch Büchner funnel. Place the bottle with the collodion membrane upon the filter paper. Pour melted vaseline, to the depth of 1 inch, between the bottle and inside of the funnel. Provide the bottle with a small mechanical stirring device.

(2) Washing and Concentration of Invertase Solution by Ultrafiltration.—Filter 4 liters of the partially purified solution

through the ultrafilter, stirring continuously, until about 1 liter remains. Wash with distilled water introduced by means of a constant-level device until the filtrate is colorless, 3 or 4 liters of wash water being required. During the entire process the invertase solution should be preserved with toluene.

The activity of the enzymes is in high degree dependent upon the pH of the medium. The curve (fig. 37) shows the relative activity of invertase as a function of pH. Michaelis and Davidson [39] found a broad optimal zone of activity for the enzyme between pH 3.5 and 5.5. Beyond these limits the activity diminished very rapidly. They found the maximum activity at pH 4.2.

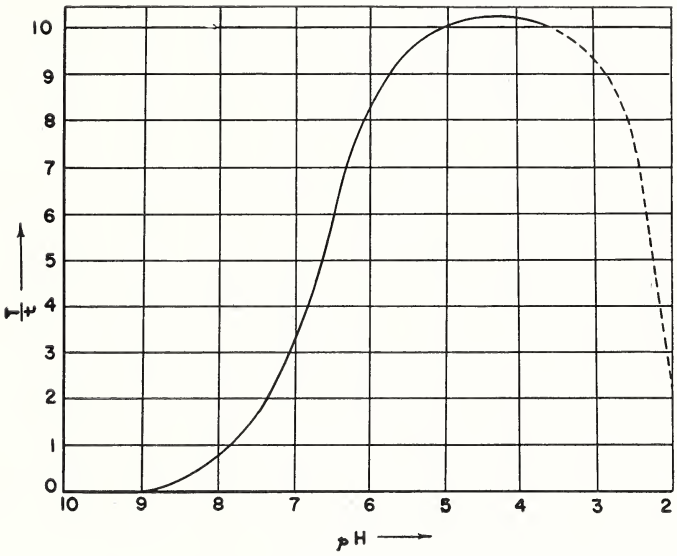


FIGURE 37.—*Activity of invertase versus* pH.

The purity of invertase preparations was expressed by O'Sullivan and Thompson in terms of the "Time Value," which represents the number of minutes required for 0.05 g of a preparation to invert to the point of zero rotation 4.0 g of sucrose in 25 ml of a solution containing 1 percent of dihydrogen sodium phosphate at 15.5° C. This point corresponds to 75.75-percent hydrolysis.

Willstätter and Kuhn [40] introduced the term "Saccharase Unit," namely the amount of enzyme having the time value 1 in 0.05 g of the invertase-containing substance acting under the definition of O'Sullivan and Thompson. Thus if a preparation containing 0.05 g of dry substance inverts sucrose to the point of zero rotation in 1 minute, it has 1 saccharase unit. Obviously, for the more active preparations smaller quantities of the enzyme are used for measurement, but the results can be calculated to the units defined above.

The practical sugar analyst is usually less concerned with the purity of his enzyme preparations than with their actual activity, which depends partly on the purity and partly on their concentration. Consequently he is not interested in expressing the activity in terms of

dry substance. The following procedure is the official method of the Association of Official Agricultural Chemists [18, p. 470.]

(3) Activity of Invertase Solution.—The following test for activity of the invertase solution is usually adequate: Dilute 1 ml of the invertase preparation to 200 ml. Transfer 10 g of sucrose (granulated sugar) to a sugar flask graduated at 100 and 110 ml, dissolve in about 75 ml of water, add 2 drops of glacial acetic acid, and dilute to the 100-ml mark. To the 100 ml of sugar solution add 10 ml of the dilute invertase solution and mix thoroughly and rapidly, noting the exact time at which the solutions are mixed. At the termination of exactly 60 minutes make a portion of the solution just distinctly alkaline to litmus paper with anhydrous sodium carbonate and polarize in a 200-mm tube at 20° C. If the invertase solution is sufficiently active, the alkaline solution will polarize approximately 31° S without correcting for the dilution to 110 ml and the optical activity of the invertase solution.

If more exact information concerning the activity of the invertase preparation is desired, determine its velocity constant as follows: Dilute 1 ml of the invertase solution to 200 ml at 20° C; place in a constant temperature bath at 20° C; and when the solution has attained the latter temperature, pipette 20 ml of it into a flask containing 200 ml of a sucrose solution (10 g per 100-ml concentration) that has been previously made distinctly acid to methyl red (corresponding to approximately pH 4.6) by the addition of acetic acid, and also brought to a temperature of 20° C in the same bath. Mix thoroughly and promptly and note the time at which the invertase solution was added. Keep the sucrose-invertase mixture in the constant-temperature bath, remove portions at the end of 15, 30, and 45 minutes; render each portion just distinctly alkaline to litmus paper with anhydrous sodium carbonate immediately after removing, and polarize at 20° C. Correct all polarizations for the polarization of the invertase solution. Calculate the velocity constant, k, for each of the polarizations (at the time, t) subsequent to the initial polarization, using the following formula:

$$k=\frac{\log_{10}1.32R_0-\log_{10}(R_t+0.32R_0)}{t},$$

in which

k=the unimolecular reaction velocity constant,

t=number of minutes elapsing from the time the invertase and sucrose solutions were mixed until inversion was stopped by addition of sodium carbonate,

R_0=initial polarization (calculated by multiplying the polarization of the sucrose solution by 10/11 and correcting for the polarization of the invertase solution),

R_t=polarization at time t.

An invertase solution of sufficient activity should yield an average value for k (for the various time periods) of at least 0.1 after multiplying the k value directly obtained by 200, in order to correct for the initial dilution of the invertase solution. The dilution of the invertase solution mentioned above is made solely for the purpose of determining its activity. The original undiluted invertase solution is used as the inverting reagent in the determination of sucrose

unless the activity of the original invertase solution greatly exceeds a k value of 0.1 and it is desirable to conserve the invertase. In this case, dilute to a k value of 0.1, which is done in the same manner as diluting other solutions to a standard strength. The activity of the invertase preparation required for rapid inversion is the same as that needed for overnight inversion, but the proportion of invertase preparation used in the former case is twice that used in the latter.

(b) PURIFICATION OF INVERTASE BY ADSORPTION

Yeast invertase, in common with other enzymes, can be absorbed on various suspended solid materials. Willstätter and Racke, whose starting point was the autolysate according to Hudson, purified the invertase by separating out impurities with kaolin which, in the crude mixture, did not adsorb invertase. They then fractionally adsorbed the enzyme with alumina in acid reaction with the addition of acetone. The eluted and purified enzyme was then found to be adsorbable by kaolin.

Adams and Hudson [41] have given in detail a method of adsorption by bentonite and subsequent elution. The following procedure is typical: A fractional autolysis of baker's yeast was prepared by treating 430 g of yeast (time value, 34.3) at 30° C with 43 ml of ether, adding after the yeast had liquified 43 ml of toluene, 430 ml of water, and 3.2 g of sodium carbonate, and 4 hours after the addition of the ether, filtering through Filter-cel, with 80 g of Filter-cel added to the mixture before filtration. The filtrate, which contained only 7.7 percent of the invertase, was discarded. To the residue was added 43 ml of toluene and 430 ml of water and autolysis was continued for 5 days at 20° C. After filtration, this autolysate was dialyzed immediately in Visking sausage casings. To a mixture of 80 ml of 0.5 percent bentonite suspension and 27 ml of a solution at pH 4.1, prepared by mixing 1 N acetic acid and 1 N sodium hydroxide was added 265 ml of the dialyzed autolysate, which contained 7.53 units of invertase per 100 ml and had a time value of 2.24 minutes. The bentonite was separated by centrifuging, washed by stirring with 200 ml of distilled water, and again centrifuged. Ninety-two percent of the invertase was adsorbed. Elution was effected by shaking gently with 3 portions, 40, 30, and 20 ml, respectively, of an acetate solution at pH 5.7, prepared from mixtures of 0.1 N acetic acid and 0.1 N sodium hydroxide solutions. The three extracts represented 57.8, 13.2, and 3.6 percent of the invertase in the original autolysate, and after dialysis had time values of 0.216, 0.215, and 0.278 minute, and contained 10.5, 2.26, and 0.64 units, respectively. The relatively small change in pH between adsorption and elution requires careful adjustment of the buffer solutions by colorimetric or electrometric methods.

Richtmyer and Hudson [42] have described an alternative adsorption method with the use of zinc sulfide precipitated directly in the invertase solution. They give in detail a typical preparation.

A baker's yeast of relatively high invertase content was allowed to autolyze fractionally, in the manner described in the process, with bentonite and the first fraction discarded. The main autolysate was dialyzed in Visking sausage casings and then represented 60 percent of the original invertase in the yeast. To 1,940 ml of this solution,

containing 110.2 invertase units, was added 1,940 ml of water, 43.5 ml of a 10-percent zinc acetate solution, 160 ml of a buffer solution at pH 4.5 (made by mixing 2 *N* sodium hydroxide and 2 *N* acetic acid), and 450 ml of a 10-percent sodium chloride solution (to prevent the zinc sulfide from becoming colloidal). Hydrogen sulfide was bubbled through the solution, and the zinc sulfide separated by centrifuging: the supernatant liquid had a pH of 4.4 and contained only 6 percent of the invertase. The zinc sulfide was washed by shaking with 1,500 ml of a 1-percent sodium chloride solution and again centrifuged. The invertase was eluted by shaking with 400, 200, and 100-ml portions, respectively, of a solution containing 1 percent of sodium chloride and 1-percent of mono- and dibasic ammonium phosphate until it had a pH of 6.1. The combined extracts, after dialysis, contained 77.6 invertase units, and had a time value of 0.20 unit.

Zinc sulfide has been used in similar fashion in purifying the dialyzed autolysates of brewer's yeast of relatively low invertase content. With these solutions a fractional adsorption with zinc sulfide is necessary, 15 to 20 percent of the invertase being discarded in the first portion. Adsorption and elution, as described, then produced invertase solutions with time value 0.21 to 0.22 minute.

(c) INVERTASE DIVISOR

Paine and Balch [43] determined with care the values of the Clerget divisor when pure sucrose is inverted with invertase. The basic value, as determined, was found to be in essential agreement with that previously measured by Zerban [44], and the values at other concentrations agreed with those of Ogilvie and of Hudson. Invertase from both top and bottom yeasts was purified by the Reynolds method [38]. Measurements were made at widely varying concentrations of sugar.

The relation between sucrose concentration and the divisor is expressed by the equation

$$\text{Divisor}=131.17+0.073c,$$

in which c is the number of grams of sucrose in 100 ml.

The basic value of the divisor thus becomes 132.12 at 20° C. Zerban found experimentally 132.10. Their concentration coefficient 0.072 is considerably at variance from the 0.082 determined by Jackson and McDonald (see p. 134).

4. DETAILED ANALYTICAL PROCEDURE

(a) CONSIDERATIONS GOVERNING THE CHOICE OF METHODS

The choice of a method of Clerget analysis depends largely upon the purpose of the analysis, the nature of the material, and upon the precision required. In general, it must be recognized that the only methods completely free from limitations are those in which the sucrose and raffinose are hydrolyzed by enzymes (see p. 159), and if high precision and perfect selectivity are required, these methods alone can insure a correct analysis. However, for the purely practical considerations of the analyst's time and the expense of the enzymes, these methods are confined largely to research projects.

The acid methods may be divided into two groups, the plain acid methods (p. 154 and 155) and the compensation methods. The compensation methods were devised, first, to eliminate errors in the analysis of products high in invert-sugar content arising from the increased rotation of the original invert sugar in the presence of acid, and second, to eliminate errors caused by the change of rotation of amino acids when highly acidified. Thus for the analysis of relatively pure samples high in invert sugar Jackson and Gillis method IV (p. 155) is to be recommended. For the analysis of samples containing both invert sugar and amino acids Jackson and Gillis method II (p. 154) is available.

There is, however, in many products of the sugar industry a group of disaccharides or oligosaccharides which are not sucrose or raffinose but are hydrolyzable by acids. The hydrolysis of these substances introduces errors into the Clerget analysis which are obviously insurmountable except by the enzyme methods.

(b) REVISED METHODS OF JACKSON AND GILLIS

(1) General Methods of Inversion.—The following methods of inversion were designed to avoid destruction of invert sugar subsequent to the completion of the inversion. There is, however, a variable amount of destruction during the process of inversion which is unavoidable. Each method, therefore, requires the use of its appropriate value of the Clerget divisor. These methods, which were determined by inversion of pure sucrose, are in general applicable to all products which do not contain considerable quantities of inorganic salts of weak acids. They can be applied to cane molasses but not to beet molasses. The latter should be inverted in a bath at 70° C, as described on page 155.

(*a*) Pipette 50 ml of the solution into a 100-ml flask, add 20 ml of water and 10 ml of hydrochloric acid ($d_{4°}^{20°}$ 1.1029 or 24.85° Brix at 20° C). Immerse in a water bath at 60° C. Agitate the solution continually for about 3 minutes, and allow it to remain in the bath for a total time of 9 minutes. Cool quickly. Basic value, 133.18.

(*b*) Pipette 70 ml of the solution into a 100-ml flask, add 10 ml of hydrochloric acid ($d_{4°}^{20°}$ 1.1029) and proceed as in (a). Basic value, 133.18.

(*c*) Pipette 75 ml of the solution, add 10 ml of hydrochloric acid ($d_{4°}^{20°}$ 1.1029) and proceed as in (a), but allow the solution to remain a total time of 9.5 minutes. Basic value, 133.18.

(*d*) Pipette 50 ml and add 20 ml of water, or pipette 70 ml of the solution, into a 100-ml flask, add 10 ml of acid, $d_{4°}^{20°}$ 1.1029, and allow to remain 30.8 hours at 20° C, 14.6 hours at 25° C, or 7.1 hours at 30° C. Basic value, 133.28.

(*e*) Walker method. Transfer 50 ml and add 25 ml of water or transfer 75 ml of the solution to a 100-ml flask and heat in a water bath to 65° C. Remove from bath, add 10 ml of hydrochloric acid ($d_{4°}^{20°}$ 1.1029), allow to cool spontaneously for 15 minutes, and cool to the temperature of polarization. In the case of low-grade products containing an excess of basic lead acetate, add previous to heating, 1 ml (or 2 ml if excess of lead is large) of the acid used for inversion. Basic value, 133.18 (tentative).

(2) METHOD I.—(Applicable to pure sucrose, or to sugar mixtures in which the impurities are unaffected optically by hydrochloric acid.)

Reagents. Hydrochloric acid ($d_{4°}^{20°}$ 1.1029 or 24.85 Brix).

Prepare a normal solution of the sample or a solution of such fractional normality as the nature of the substance will permit. Defecate, if necessary, with basic lead acetate in the usual manner, making to volume at the temperature at which the observations are to be made, and filter.

(If desired, the excess of lead may be removed at this point by the addition of pulverized potassium or sodium oxalate. However, it is necessary that the whole filtrate be treated by the deleading reagent, since the latter exerts an effect upon the rotation of invert sugar which should be as far as possible offset by a similar effect on sucrose.) Polarize the solution to obtain the direct reading and, if necessary, correct to the value which would have been obtained if 26 g of the sample were taken in 100 ml of solution.

To obtain the invert polarization, invert as described on page 153. make to a volume of, 100 ml at the temperature at which the observations are to be made, and polarize. Correct the observed polarization to that of a normal solution. The algebraic difference between the two polarizations corrected for dilution gives the value $P-P'$. Determine by refractometer the dry-substance concentration of the original sample and calculate the weight of solids, m, taken for the invert polarization.

Calculate the percentage of sucrose by the formula

$$S=\frac{P-P'}{\text{Basic value}+0.0794(m-13)-0.53(t-20)}.$$

The basic value is 133.18 for inversion at 60° C or 133.28 for room-temperature inversion.

(3) METHOD II.—(General method applicable to all products.) Reagents. Hydrochloric acid ($d_{4°}^{20°}$ 1.1029 or 24.85 Brix); ammonium hydroxide solution, 5 to 6 N; solution of ammonium chloride containing 226 g per liter; pulverized potassium or sodium oxalate.

Ascertain by at least three concordant titrations in the presence of methyl orange the volume of the ammonia solution required to neutralize 10 ml of the hydrochloric acid.

Prepare a normal solution of the sample or a solution of such fractional normality as the nature of the substance will permit. Defecate, if necessary, with basic lead acetate in the usual manner, making to volume at the temperature at which the observations are to be made. Filter.

(If desired, the solution may at this point be freed from lead; but if this is done, the deleading reagent must be added to the whole filtrate. Finely pulverized potassium oxalate in minimum quantity is added until precipitation is complete. Filter. If this procedure is omitted, the lead is precipitated satisfactorily by the chlorides added later.)

Pipette into two 100-ml flasks two equal volumes of the filtrate (50, 70, or 75 ml).

For the direct polarization, add to 1 portion 15 ml of the ammonium chloride solution or 3.392 g of dry ammonium chloride. Make to volume at the temperature at which the observations are to be made; filter, if necessary, and polarize.

For the invert polarization, add hydrochloric acid to the other portion and invert by one of the methods described on page 153. Cool quickly. After the solution has become quite cold add from a burette during continual shaking, the precisely determined volume of ammonia required to neutralize the acid. Adjust the temperature, make to volume, filter, if necessary, and polarize at carefully controlled temperature. Correct both polarizations to the normal weight of sample.

Calculate the percentage of sucrose by the formula

$$S=\frac{P-P'}{\text{Basic value}+0.0794(m-13)-0.53(t-20)},$$

in which m is the weight of dry substance taken for invert polarization. The basic value of the divisor is 133.27 for 60° C inversion or 133.37 for room-temperature inversion.

(4) Method iv.—(Applicable in the presence of invert sugar, but inapplicable in the presence of optically active non-sugars which change rotation with acidity. In principle sodium chloride equalizes the effect of hydrochloric acid on invert sugar present as an impurity.)

Prepare a normal solution of the sample or a solution of such fractional normality as the nature of the substance will permit. Defecate, if necessary, with basic lead acetate in the usual manner, making to volume at the temperature at which the observations are to be made. Filter.

(If desired, the excess of lead may be removed at this point. Add pulverized potassium or sodium oxalate to complete precipitation of lead. The deleading reagent should be added to the whole filtrate. If the deleading is omitted, the lead is satisfactorily removed by the chlorides subsequently added.)

Pipette two 70-ml (or 50 ml+20 ml of water) portions of the clear filtrate into two 100-ml flasks. If preferred, 75-ml portions may be taken.

To 1 portion add 2.315 g of sodium chloride or 7.145 ml of a saturated sodium chloride solution or 10 ml of a solution containing 231.5 g per liter; make to volume at the temperature at which the observations are to be made and polarize.

To the other portion add hydrochloric acid and invert by one of the methods described on page 153. Cool and make to volume at the temperature at which the observations are to be made. Polarize. Correct both rotations to the normal weight of sample.

Calculate the percentage of sucrose by the formula

$$S=\frac{P-P'}{\text{Basic value}+0.0794(m-13)-0.53(t-20)},$$

in which m is the weight of dry substance taken for the invert polarization. The basic value is 132.56 for 60° C inversion or 132.66 for room-temperature inversion.

(c) ACID METHODS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

(1) Determination of Sucrose by Polarization Before and After Inversion With Hydrochloric Acid.—(In the presence of much levulose, as in honeys, fruit products, sorghum sirup, cane sirup,

and molasses, the optical method for sucrose, requiring hydrolysis by acid, gives erroneous results.)

Direct reading.—Proceed as directed under "Direct reading," page 157.

Invert reading.—Pipette a 50-ml portion of the lead-free filtrate into a 100-ml flask and add 25 ml of water. Then add, little by little, while rotating the flask, 10 ml of hydrochloric acid (sp. gr. 1.1029 at 20°/4° or 24.85° Brix at 20°C). Heat a water bath to 70°C and regulate the burner so that the temperature of the bath remains approximately at that point. Place the flask in the water bath, insert a thermometer, and heat with constant agitation until the thermometer in the flask indicates 67°C. (This preliminary heating period should require from 2½ to 2¾ minutes). From the moment the thermometer in the flask indicates 67°C, leave the flask in the bath for exactly 5 minutes longer, during which time the temperature should gradually rise to about 69.5°C. Plunge the flask at once into water at 20°C. When the contents have cooled to about 35°C, remove the thermometer from the flask, rinse it, and fill almost to the mark. Leave the flask in the bath at 20°C for at least 30 minutes longer and finally make up exactly to volume. Mix well and polarize the solution in a 200-mm tube provided with a lateral branch and a water jacket, maintaining a temperature of 20°C. This reading must also be multiplied by 2 to obtain the invert reading. If it is necessary to work at a temperature other than 20°C, which is permissible within narrow limits, the volumes must be completed, and both direct and invert polarizations must be made at exactly the same temperature.

Calculate sucrose by the following formula:

$$S=\frac{100(P-I)}{143+0.0676(m-13)-0.53t},$$

in which

S=percentage of sucrose,
P=direct reading, normal solution,
I=invert reading, normal solution,
t=temperature at which readings are made,
m=grams of total solids from original sample in 100 ml of the invert solution.

Determine with the refractometer the total solids as percentage by weight, as directed on page 258, and multiply this figure by the density at 20°C, as obtained from table 113, page 626.

Inversion at room temperature.—The inversion may also be accomplished as follows: (1) To 50 ml of the clarified solution, freed from lead, add 10 ml of hydrochloric acid (sp. gr 1.1029 at 20°/4° or 24.85° Brix at 20°C) and set aside for 24 hours at a temperature not below 20°C; or, (2) if the temperature is above 25°C, set aside for 10 hours. Make up to 100 ml at 20°C and polarize. Under these conditions, the formula must be changed to the following:

$$S=\frac{100(P-I)}{143.2+0.0676(m-13)-0.53t}.$$

(2) Determination of Sucrose and Raffinose by Polarization Before and After Inversion With Hydrochloric Acid.—(Of value chiefly in the analysis of beet products.) If the direct reading is

more than 1° higher than the percentage of sucrose, as calculated by the formulas given on p. 156, raffinose is probably present. Calculate sucrose and raffinose by the following formulas:

When the polarizations are made at 20° C,

$$S=\frac{0.514P-I}{0.844} \text{ and } R=\frac{0.33P+I}{1.563},$$

in which

P=direct reading, normal solution,
I=invert reading, normal solution,
S=percentage of sucrose,
R=percentage of anhydrous raffinose.

The following formulas are applicable at all temperatures:

$$S=\frac{P(0.478+0.0018t_2)-I(1.006-0.0003t_1)}{(0.908-0.0032t_2)\ (1.006-0.0003t_1)},$$

$$R=\frac{P(0.43-0.005t_2)+I(1.006-0.0003t_1)}{(1.681-0.0059t_2)\ (1.006-0.0003t_1)},$$

in which

P= direct reading, normal solution,
I= invert reading, normal solution,
S= percentage of sucrose,
R= percentage of anhydrous raffinose,
t_1=temperature of the direct polarization,
t_2=temperature of the invert polarization.

See also discussion of Creydt's raffinose formula on page 143.

(d) INVERTASE METHODS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

(1) Determination of Sucrose.

Direct reading.—Dissolve the double-normal weight of the substance (52 g), or a fraction thereof, in water in a 200-ml volumetric flask; add the necessary clarifying agent, avoiding any excess; shake, dilute to the mark with water, mix well, and filter, keeping the funnel covered with a watch glass. Reject the first 25 ml of the filtrate. If a lead clarifying agent was used, remove the excess lead from the solution when sufficient filtrate has collected, by adding anhydrous sodium carbonate a little at a time, avoiding any excess; mix well and filter again, rejecting the first 25 ml of the filtrate. (Instead of weighing 52 g into a 200-ml flask, two 26-g portions may be diluted to 100 ml each and treated exactly as described. Depending on the color of the product, multiples or fractions of the normal weight may be used and the results reduced by calculation to the basis of 26 g in 100 ml.) Pipette one 50-ml portion of the lead-free filtrate into a 100-ml flask, dilute with water to the mark, mix well, and polarize in a 200-mm tube. The result, multiplied by 2, is the direct reading (P of formula given below), or polarization before inversion. (If a 400-mm tube is used the reading equals P.) If there is a possibility of mutarotation, allow sufficient time for its completion.

Invert reading.—First determine the quantity of acetic acid necessary to render 50 ml of the lead-free filtrate distinctly acid to methyl

red indicator, pH 4.4; then to another 50 ml of the lead-free solution in a 100-ml volumetric flask, add the requisite quantity of acid and 5 ml of the invertase preparation, fill the flask with water nearly to 100 ml, and let stand overnight (preferably at a temperature not less than 20° C). Cool, and dilute to 100 ml at 20° C. Mix well and polarize at 20° C in a 200-mm tube. If there is doubt as to the completion of the hydrolysis, allow a portion of the solution to remain for several hours and again polarize. If there is no change from the previous reading, the inversion is complete. Carefully note the reading and temperature of the solution. If it is necessary to work at a temperature other than 20° C, which is permissible within narrow limits, complete the volumes and make both direct and invert readings at the same temperature. Correct the polarization for the optical activity of the invertase solution and multiply by 2. Calculate the percentage of sucrose by the formula

$$S=\frac{100(P-I)}{142.1+0.073(m-13)-t/2},$$

in which

S=percentage of sucrose,
P=direct reading, normal solution,
I=invert reading, normal solution,
t=temperature at which readings are made,
m=g of total solids from original sample in 100 ml of the invert solution.

Determine with the refractometer the total solids as a percentage by weight, as directed on page 258, and multiply this figure by the density at 20° C, as obtained from table 113, p. 626.

Rapid inversion at 55° to 60° C.—If more rapid inversion is desired, proceed as follows: Prepare the sample as directed under "direct reading," p. 157, and to 50 ml of the lead-free filtrate in a 100 ml volumetric flask add glacial acetic acid in sufficient quantity to render the solution distinctly acid to methyl red, pH 4.4. The quantity of acetic acid required should be determined before pipetting the 50-ml portion, as described in the preceding paragraph. Then add 10 ml of invertase solution, mix thoroughly, place the flask in a water bath at 55° to 60° C, and allow to stand at that temperature for 15 minutes with occasional shaking. Cool, add sodium carbonate until distinctly alkaline to litmus paper, dilute to 100 ml at 20° C, mix well, and determine the polarization at 20° C in a 200-mm tube. Allow the solution to remain in the tube for 10 minutes and again determine the polarization. If there is no change from the previous reading, the mutarotation is complete. Carefully note the reading and the temperature of the solution. Correct the polarization for the optical activity of the invertase solution and multiply by 2. Calculate the percentage of sucrose by the formula given above.

If the solution has been rendered so alkaline as to cause destruction of sugar, the polarization, if negative, will in general decrease, since the decomposition of fructose ordinarily is more rapid than that of the other sugars present. If the solution has not been made sufficiently alkaline to complete mutarotation quickly, the polarization, if negative, will in general increase. As the analyst gains experience he may omit the polarization after 10 minutes, if he has satisfied himself

that he is adding sodium carbonate in sufficient amount to complete mutarotation at once without causing any destruction of sugar during the period intervening before polarization.

(2) Sucrose and Raffinose by Polarization Before and After Treatment With Two Enzyme Preparations.

Invertase solution (top-yeast extract).—Prepare as directed on page 147. This solution should be free from the enzyme melibiase. Its invertase activity should be at least as great as that used for the determination of sucrose in the absence of raffinose.

Invertase-melibiase solution (bottom-yeast extract).—Prepare as directed on page 147, using bottom fermenting yeast (brewers' yeast) instead of bakers' yeast. The invertase activity should be at least as great as that from the top-yeast extract.

Test the melibiase activity of the solution as follows. Add 2 ml of the solution to be tested to 20 ml of a weakly acid melibiose solution polarizing +20.0° S and allow to stand 30 minutes at about 20° C. Then add sufficient sodium carbonate to render the solution slightly alkaline to litmus paper. A preparation suitable for the overnight hydrolysis of solutions containing not more than 0.2 g of raffinose in 100 ml should hydrolyze 35 percent of the melibiose present under the conditions mentioned; a preparation suitable for the overnight hydrolysis of solutions containing not more than 0.65 g of raffinose in 100 ml should produce 50-percent hydrolysis of melibiose; and a preparation suitable for the overnight hydrolysis of solutions containing 0.65 to 1.3 g of raffinose in 100 ml should hydrolyze at least 70 percent of the melibiose present under the above condition. The polarizations that correspond to 35-, 50-, and 70-percent hydrolysis of a melibiose solution polarizing, before hydrolysis, +20° are +16.4°, +14.9°, and +12.9° S, respectively.

Determination.—In the analysis of sugar-beet products, weigh the quantity of material specified in table 19, transfer to a 300-ml volumetric flask, add the quantity of basic lead acetate solution indicated in the table, and dilute to volume at 20° C. Mix thoroughly and filter through fluted paper in a closely covered funnel, rejecting the first 25 ml of filtrate. When sufficient filtrate has collected, remove the lead from the solution by adding ammonium acid phosphate in as small excess as possible (see table 19). This condition is readily determined, after a little practice, by the appearance of the lead phosphate precipitate, which usually flocculates and settles rapidly in the presence of a slight excess of the salt. Mix well and filter, again rejecting at least the first 25 ml of the filtrate. Make a direct polarization in a 200-mm tube at 20° C, unless the solution contains an appreciable quantity of invert sugar, in which case pipette a 50-ml portion of the lead-free filtrate into a 100-ml flask, dilute with water to the mark, mix well, and polarize at 20° C, preferably in a 400-mm tube. This reading, calculated to the normal weight of 26 g in 100 ml and 200-mm tube length, is the direct reading (P) of the formula given in table 19 for polarization before inversion.

Transfer two 50-ml portions of the lead-free filtrate to 100-ml flasks. To one add 5 ml of invertase solution (top-yeast extract), page 147, and to the other add 5 ml of invertase-melibiase solution (bottom-yeast extract), page 147, let stand overnight at atmospheric temperature (preferably not below 20° C), dilute to volume, mix well, and polarize at 20° C, preferably in a 400-mm jacketed tube. If a

TABLE 19.—*Quantity of sample and reagents required for clarification and deleading of beet sugar-house products*

Material	Quantity per 100 ml	Basic lead acetate (55° Brix)	Ammonium dihydrogen phosphate
	g	*ml*	*g*
Cossettes [1]	13	3	0.2
Pulp	100 ml	2 to	.2
Lime cake or sewer [3]	26.5 [2]	1.5 [4]	([4])
Thin juice	52	2	.2 to 0.3
Thick juice	26	4	.3 to .4
White massecuite	13 or 26	3 or 6	.3 to .7
High wash sirup	13 or 26	3 or 6	.3 to .7
High green sirup	13 or 26	5 or 10	.3 to .7
Raw or remelt massecuite	13	6	.3 to .4
Raw or remelt sugar	26	3 to 4	.3 to .4
Sugar melter	26	2 to 3	.3 to .4
Low wash sirup	13	8 to 10	.4 to .5
Low green sirup or molasses	13	10	.4 to .5
Saccharate cakes and milk (carbonated)	26	4 to 6	.3 to .4
Steffen waste and wash waters [3]	78 or 50 ml	2 to 3	.2

[1] Usual method of extraction, 26 g in 201.2 ml.
[2] Dilute to 110 ml.
[3] Neutralize with acetic acid before adding basic lead acetate.
[4] Lime in solution will be precipitated partly by the phosphate, and it is necessary to add sufficient phosphate to complete the precipitation of both the lead and lime salts; hence no definite quantity can be specified.

rapid hydrolysis is desired, add 10 ml of each of the enzyme solutions to the 50-ml portions of deleaded filtrate in 100-ml flasks, and place in a water bath at 50° to 55° C for 40 minutes. Then add sodium carbonate until the solution is slightly alkaline to litmus paper, dilute to volume at 20° C, mix well, and polarize at 20° C, preferably in a 400-mm tube. Correct the invert readings for the optical activity of the enzyme solution, and calculate the polarization to that of a normal-weight solution of 26 g in 100 ml; also calculate the reading to a 200-mm tube length, if necessary.

Calculate the percentages of anhydrous raffinose and sucrose from the formula

$$R=1.354\ (A-B),$$

$$S=\frac{(P-2.202A+1.202B)100}{132.12-0.00718[132.12-(P-2.202A+1.202B)]},$$

in which

R=percentage of raffinose,
S=percentage of sucrose,
P=direct polarization, normal solution,
A=corrected polarization after top-yeast hydrolysis, normal solution,
B=corrected polarization after bottom-yeast hydrolysis, normal solution. A and B are treated algebraically.

(e) DOUBLE-ACID METHOD OF OSBORN AND ZISCH

Osborn and Zisch [31], finding the double-enzyme method reliable in the analysis of beet products, but impracticable because of the expense of the enzymes and the difficulty of obtaining satisfactory preparations, sought to modify the methods of acid hydrolysis in such manner as to make them suitable for routine analysis. They pointed out that the direct polarization is the resultant rotation of sucrose,

raffinose, and a group of optically active nonsugars consisting mainly of amino acids. The rotation of the latter group they called the N value. The presence of three unknown quantities required three equations for their solution. They found, in agreement with Paine and Balch [45] and with Zerban [46], that the rotation of the nonsugars became zero in strongly acid solution but was restored to its original value by neutralization. If, therefore, the invert polarization was observed in both acid and neutral solution, the difference between the two readings became a measure of N. This fact had previously been stated by Zerban, who observed that the difference between Jackson and Gillis methods II and IV was a measure of the optically active amino compounds, but he did not apply the principle to a quantitative method of analysis.

(1) *Procedure.*—Transfer 130 g of the sample, or its equivalent, to a 500-ml Kohlrausch flask, add the necessary basic lead acetate, and make to 400 to 450 ml with water. Deaerate under vacuum until all visible gas bubbles are removed, using a few drops of ether or amyl alcohol to break the foam, if necessary. Make to 500 ml at 20° C, mix, and filter. Delead the filtrate with the minimum of powdered ammonium dihydrogen phosphate, and filter, using a little filter aid if desired. Polarize in a 200-mm tube to obtain the direct polarization, P.

Pipette 50 ml of the deleaded filtrate into each of two 100-ml Kohlrausch flasks. Add 15 ml of water and heat to 68° to 69° C in a 70° C water bath. Remove from bath, and immediately add 10 ml of hydrochloric acid ($d\,{}^{20°}_{4°}$ 1.1029). Allow to cool spontaneously for 2 hours, and then cool to 20° C. Make the one invert to 100 ml at 20° C, mix, filter if necessary, and polarize at 20° C in a 400-mm tube, the reading being the invert polarization, I. To the second invert, add 1 or 2 drops of 0.2 percent methyl red indicator solution and neutralize with 6.34 N ammonium hydroxide, adding the ammonia very slowly from a burette while constantly whirling the flask. Then add exactly 1 ml in excess. Make to 100 ml at 20° C, filter if necessary, and polarize in a 400-mm tube to obtain the neutralized invert polarization, I'.

The N value, sucrose, and raffinose are then calculated by the formulas

$$N = I' - I + K,$$

$$P' = P - N,$$

$$S = \frac{0.514P' - I}{0.514 + (0.321 + 0.00009S)} = \frac{0.514P' - I}{0.835 + 0.00009S},$$

$$R = 0.54\,(P' - S),$$

in which

N = polarizing effect of the optically active nonsugars,
P' = true direct polarization of the raffinose and sucrose,
S = percentage of sucrose,
R = percentage of raffinose,
K = neutralization correction $= 0.0047S + 0.00017Sv$, in which v is the number of milliliters of basic lead (55 Brix) added per 100 ml. It is satisfactory to use P instead of S.

NOTES.—The correction, K, is required because the negative rotation of invert sugar is enhanced to a higher negative value upon neutralization with ammonia. It also includes the effect of ammonium acetate, which varies with the volume of

lead acetate added. The numerical values of K are conveniently tabulated in the original article.

Not more than a few drops of amyl alcohol should be added, since it is optically active.

Cover filters during filtration, and discard the first 10 to 15 ml of each filtrate.

No more ammonium phosphate than necessary should be used, since 1 g per 100 ml depresses the direct polarization by 0.35°S.

The authors restrict the method to beet products subsequent to the carbonation stage. It proved applicable to such products in a wide geographical territory, centering in Colorado, but not to those from California. It cannot be applied to any mixture containing invert sugar.

With the application of the method thus restricted, the authors found excellent agreement between this and the double-enzyme method. It proved inexpensive and well adapted to routine analysis. The average value of N for 28 samples of beet molasses from both Steffen and non-Steffen factories, proved to be —1.62 by the double-acid method, and —1.71 by the double-enzyme method. The average sucrose content agreed within 0.01 percent and raffinose within 0.06 percent. The International Commission for Uniform Methods of Sugar Analysis in 1936 found the method too restricted in its application to justify adoption. It is to be noted, however, that the method of Osborn and Zisch is the first successful attempt to find the necessary third equation for the solution of the three unknown quantities in the composition of beet products, even though somewhat restricted in its application.

(f) METHODS OF OTHER NATIONS

Much effort has been devoted to the elimination of the effect of optically active amino acids on the Clerget analysis. These nitrogenous substances exhibit one rotatory power in a neutral or alkaline medium and a quite different one in acid medium. It was, therefore, recognized early that both direct and invert polarizations must be made in the same medium in respect to hydrogen-ion concentration. These efforts have been directed in two ways, namely to read both solutions in neutral solution or both in acid solution.

In the early experiments, Pellet sought to equalize the effect by acidifying the direct polarization with sulfur dioxide. The acidity of such a solution, however, is too weak to affect the rotation of the amino acids to the same degree as the hydrochloric acid of the invert polarization. Andrlik observed the direct polarization in the presence of hydrochloric acid to which urea was added in such quantity as to slow the hydrolysis of sucrose. This interesting expedient has caused much discussion but has not been put into general use.

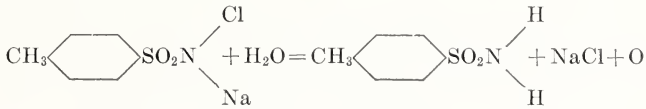
A more promising method was proposed by Stanek [47], who inverted with hydrochloric acid in the usual way, but upon completion of the inversion added potassium citrate stoichiometrically equivalent to the hydrochloric acid, causing the formation of potassium chloride and citric acid. To the direct polarization was added the same mixture, it being determined that the citric acid, having but 1.72 percent of the inverting power of hydrochloric acid, produced no appreciable effect upon the sucrose. Stanek found a Clerget divisor of 132.66 at 20° C. The official methods in Czechoslovakia specify the Stanek method, with the rounded-off divisor 132.6 for sucrose determinations in beet molasses.

Babinski and Ablamowicz [48] utilized the Stanek principle, but substituted sodium acetate for potassium citrate. The method was officially adopted in Poland, with a basic value of 131.46 for the divisor.

Both Stanek and Babinski clarified the solutions by the addition of saturated (3-percent) bromine water. This is stated to give good clarification and rapid filtration. The precipitate amounts, with molasses, to about 0.1 g and, therefore, its influence on the con-

centration of the sample is negligible. The objecton to its use is the disagreeable odor and corrosive effect of free bromine.

In order to make use of the Stanek-Babinsky principle, Schlemmer [49] studied the clarification with Aktivin or Chloramin-T, which reacts with water as follows:



In combination with sodium bromide, the oxygen set free releases two atoms of bromine from the sodium bromide. The released bromine clarifies the solution which, after filtration, remains clear for about ½ hour. The precipitate from beet molasses weighs about 0.15 g. No odor of bromine is appreciable.

The following solutions are required:

(a) Hydrochloric acid, 18.38 percent; $d=1.092$.

(b) Sodium acetate, 400 g; and potassium bromide, 50 g in 1 liter.

(c) A solution containing about 15 percent of Chloramin-T.

(d) A mixture of solutions (a) and (b) in the ratio 20 ml of (b) to 10 ml. of (a).

Procedure for beet molasses.—Transfer 52 g of molasses to a 200-ml flask and fill to the mark at 20°. Mix thoroughly, and pipette two 50-ml portions to 100-ml flasks. To one add 30 ml of solution (*d*). Add 10 ml of solution (*c*). Adjust to 20°, mix, filter, and polarize at 20°. To the other solution add 10 ml of solution (*a*), invert according to Schrefeld's method (page 129), cool, and add 20 ml of solution (*b*). Add in 3 portions 10 ml of solution (*c*), make to volume at 20° C, filter, and polarize at 20°.

Schlemmer determined the value of the divisor for one-half-, one-fourth-, and one-eighth-normal solutions of sucrose and, surprisingly enough, found no variation with concentration. He reported the values 131.98 for pure sucrose and 131.75 at 20° for final beet molasses. Apparently no measures are taken in these methods to evaluate the raffinose content of beet products.

Steuerwald [50] devised a method, extensively used in the Dutch East Indies, in which the inversion is carried out at room temperature by hydrochloric acid of such high concentration that the reaction is completed without the attention of the analyst within 2 or 3 hours. The direct polarization is observed in the usual manner.

For the invert polarization, measure 50 ml of the clarified filtrate with a 100-ml flask, and add 30 ml of hydrochloric acid of 1.1 sp gr (acid of 1.188 sp gr diluted with an equal volume of water). Set aside for 3 hours if the temperature is between 20° and 25° C or for 2 hours if above 25°. Dilute the solution to 100 ml and polarize at a carefully observed temperature. Calculate both polarizations in terms of the normal weight of the sample in 100 ml.

Calculate the percentage of sucrose by the formula

$$S=\frac{100(P-P')}{145.54+0.0676(m-13)-0.53t}.$$

Jackson and Gillis [3, p. 168] showed that the high basic value of the Steuerwald divisor was consistent with their own and other values of the divisor if the effect of the acid is considered.

If the sample contains a considerable quantity of invert sugar it would seem probable that the Steuerwald method would yield high results for sucrose, since the effect of the acid is to increase greatly the negative rotation of original invert sugar in the invert polarization. This effect is uncompensated.

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IX. CHEMICAL METHODS FOR THE DETERMINATION OF REDUCING SUGARS

1. THEORETICAL AND GENERAL

(a) INTRODUCTION

The history of the growth of reducing-sugar analysis begins in 1815, when Vogel showed that the reddish precipitate produced by boiling copper acetate with honey was not metallic copper, as had previously been supposed, but was cuprous oxide. From this small beginning the development was slow, with the major steps in progress decades apart. In 1841 Trommer found that, by making the copper solution alkaline, not only was a differentiation of sugars made possible, but the sensitivity was increased. In 1838 a French society offered a prize for a successful method of quantitative estimation of sugar, and an award of a portion of the prize was made in 1844 to Barreswil, who adapted Trommer's qualitative method to a quantitative method of analysis. He also showed that cane sugar could be determined by observing its reducing power before and after inversion.

In 1849 H. Fehling [1] worked out with great care the details of the method, giving some account of the stoichiometrical equivalents. Fehling believed that one molecule of glucose reduced five equivalents of copper, not recognizing that the reaction is quantitative only within narrow limits of concentration and time of reaction. Fehling's method proved satisfactory in respect to sensitivity and reproducibility of analysis, but the copper solution was unstable.

Soxhlet [2] effected still further improvements, utilizing the same reagents in the same proportions as Fehling, but preserving the copper solution and the alkaline tartrate solution in separate containers until required for analysis. This solution and method have been utilized up to the present day.

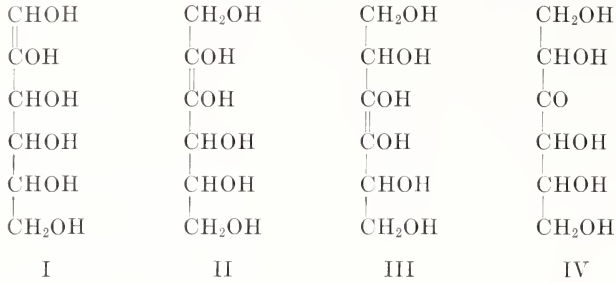
(b) REDUCING SUGARS IN ALKALINE SOLUTION

When glucose, levulose, or mannose is subjected to the action of dilute alkali in aqueous solution, the three sugars undergo a mutual conversion into each other until an equilibrium is established.[8] The composition of this mixture is the same regardless of the sugar taken as the starting material. These relations were shown in a very striking manner by Lobry de Bruyn and van Ekenstein [3], who applied the same conditions to other sugars and found equilibria between galactose, talose, and tagatose, and in many other systems. This reaction is a perfectly general one and is of practical value for the conversion of readily available sugars into new sugars or into sugars of less common occurrence.

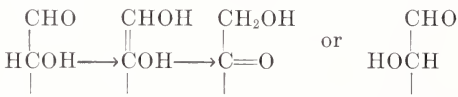
The mechanism of the reaction has been studied extensively. Nef [4] showed that a hexose in alkaline solution was converted into a 1,2-enediol (I). He accounted for the final products by assuming that, to this enediol, water can be added in three different ways: The hydroxyl may attach to the terminal carbon atom, yielding the aldehyde group; the hydrogen attaching to the second carbon atom

[8] The reactions occurring in alkaline solution, and briefly indicated in this and succeeding paragraphs, are too involved to describe in detail. The purpose here is to show the nature of the reactions rather than their accurate course.

by rupture of either one of the bonds, yielding either of two aldoses; or the hydroxyl may attach to the second carbon atom and yield, with elimination of water, the ketose.



Wolfrom and Lewis [5], working with tetramethylglucopyranose, observed that true equilibrium was apparently established between glucose and mannose but that no ketose appeared to be formed. On this basis they considered the reaction to consist of a simple enolization and regeneration of the carbonyl group. Thus



On more prolonged action of the alkali, the enediols may descend to the 2,3 position (II), or to the 3,4 position (III). The latter yields a 3-ketose, known as glutose (IV), which, since the hydroxyl on the second carbon may previously have undergone transformation, occurs in two forms, alpha and beta glutose. As a result of overliming or of high local concentrations of lime in the processes of cane-sugar manufacture, glutose is frequently found in cane molasses to the extent of several percent. It has about one-half the reducing power of dextrose and is unfermentable by yeast.

If the alkalinity of the solution is greatly increased, still more deep-seated changes occur in the reducing-sugar molecule, and saccharinic acids and their lactones are formed, of which there are 24 isomers theoretically possible.

In the presence of oxidizing agents, such as cupric salts in alkaline solution, the enediols are strongly reducing and can take up oxygen at the expense of copper, thereby reducing it to cuprous oxide. According to Nef's theory [4], a momentary dissociation of the molecule occurs at the position of the double bond and each fragment takes up oxygen to yield the corresponding hydroxy acid. Since the enediol may, at the time the molecule is ruptured, be either at the 1,2; 2,3; or 3,4 position, and since the hydroxyls may have altered their relative position, the number of different acids produced is large. Mannose, glucose, and levulose all give the same oxidation products in the presence of sodium and cupric hydroxides, namely carbon dioxide, formic, glycolic, *d,l*-glycerinic, *l*-threonic, and *d*-erythronic, *d*-mannonic, *d*-gluconic, α-hydroxy-methyl-*d*-arabonic, and the pentonic acids.

(c) COPPER-TARTRATE COMPLEXES

If a solution of copper sulfate is added to a chemically equivalent solution of sodium tartrate, cupric tartrate is precipitated and may be

isolated. If to this cupric tartrate one equivalent of sodium hydroxide is added, the insoluble cupric tartrate dissolves to form a deep-blue solution that is neutral to litmus, indicating that the whole cupric tartrate residue has behaved as an anion to neutralize the alkali. This is further shown by the migration of copper to the anode upon electrolysis. Cupric salts behave in a similar manner with many other substances, such as citrates, oxalates, salicylates, carbonates, glycerol, and cane sugar.

Fortunately, this property of forming soluble complexes is confined to the cupric salts, for, when under the influence of reducing reagents the copper is reduced to the cuprous state, the latter, being unable to form such complexes, precipitates in the alkaline solution in the form of cuprous oxide.

For the preparation of reagents suitable for sugar analysis, the alkali must be in excess of one equivalent of alkali to one of cupric tartrate, for the enolization occurs only in alkaline solutions.

(d) CLASSIFICATION OF REDUCING SUGARS

The sugar group may be classified with respect to reducing power into three classes: Nonreducing sugars, such as sucrose and raffinose; monosaccharides, such as glucose, levulose, and xylose; reducing disaccharides, such as lactose and maltose. The nonreducing sugars lack the free aldehyde or lactonyl structure which is characteristic of reducing sugars. The reducing disaccharides possess the reducing group on only one of the hexose residues. During the reduction it is this residue which is mainly subject to oxidation; consequently the disaccharides have but little more than half the reducing power possessed by the monosaccharides.

(e) MODERN INVESTIGATIONS

Subsequent to the work of Fehling and of Soxhlet, which laid the foundation for accurate analytical processes, variations of procedure and of composition of the alkaline copper solutions were proposed in great number in an effort to effect still further improvements. Many of these modifications served a useful purpose in their day, but almost all have been displaced in modern times by the unified methods. The early tendency was to devise a particular method for each sugar under examination. This necessitated the use of different reagents and different procedures and, when the sample contained a mixture of sugars, rendered an interpolation of copper equivalents impossible. These difficulties led to the establishment of unified methods of procedure, whereby the same reagents and procedure were used, regardless of the nature of the sugar. Empirical copper equivalents were then determined for the sugars of common occurrence. This unification of methods has caused most of the older methods to become obsolete. However, the latter are of historical interest and, in some instances, of intrinsic value, and they are frequently useful to the specialized worker.[9]

Quisumbing and Thomas [6] have investigated the reduction reaction in detail, studying in particular the results caused by varying the

[9] A list of the many alkaline copper solutions which were devised during this early period is given in Wiley's Agricultural Analysis, 1st ed. vol. 3, p. 183. Some of the more valuable early methods are described in Browne's Handbook of Sugar Analysis, 1st ed., p. 388 (1912).

composition of the alkaline copper reagent. The nature and concentration of alkali influence both the amount of reduction and the physical character of the cuprous oxide. Sodium hydroxide and potassium hydroxide solutions of equivalent concentrations yield practically the same reduction with the hexoses, but potassium hydroxide causes a higher reduction with maltose than sodium hydroxide. In general, sodium hydroxide yields the more satisfactory precipitate in respect to physical characteristics.

When the concentration of alkali is varied, the amount of copper reduced by sugars rises sharply as the alkalinity is increased from zero and reaches a maximum at about 1.6 N, the normality being referred to the mixed copper reagents. Around this concentration of alkali the curve is relatively flat, so that considerable variations in alkalinity produce inappreciable effects. The Fehling-Soxhlet tartrate solution, which is so commonly employed, is about 1.2 N with respect to alkali. It has not exactly the optimum composition, but it is nevertheless situated on a portion of the curve at which the amount of copper precipitated varies but slightly with the concentration of alkali. It is remarkable that Fehling, groping about in an effort to devise a system of analysis, should have aimed so nearly true. At higher concentrations of alkali the amount of copper reduced diminishes, slightly in the case of hexoses, considerably more with maltose and lactose.

Since, as was indicated in a previous paragraph, the reactions of reducing sugars are very complex, it follows that there is no exact stoichiometrical relation between the sugar and reduced copper. In the early stages of the reaction very rapid changes occur, and in fact the maximum rate of reduction occurs at about 75° C. The products of these first stages of oxidation are also capable of reducing copper but at a much slower rate. The result is that the reduction of copper continues, even if the time of reaction is greatly prolonged. All practical methods therefore necessarily require that the time of reaction be strictly defined. The time of reaction may be arbitrarily chosen, but must be definite. Since the reaction starts at a relatively low temperature, the preliminary stages of heating are important and the conditions should be carefully controlled.

As is well known, sucrose possesses an appreciable reducing power in alkaline solution. The source of its reducing action is obscure but is generally ascribed to a slight hydrolysis by hydroxyl ions. The reducing power increases rapidly with the alkalinity of the solution. Hence the Soxhlet and similar solutions containing caustic alkali are more strongly reduced by sucrose than those which contain alkali carbonates. In the analysis of relatively pure samples of sucrose, the reduction by the sucrose itself is frequently of such magnitude that it greatly masks that of the contaminating reducing sugar. This has led from very early times to the employment of the more weakly alkaline carbonate solutions for the analysis of sucrose samples. Even with such solutions, sucrose exhibits a measurable reducing power. In the preparation of sucrose for the establishment of polariscopic standards, Bates and Jackson [7] showed that the reducing reaction of sucrose was different from that caused by true reducing sugar, for sucrose yielded weights of reduced copper increasing linearly with the time of reaction, while the reduction by reducing sugar was practically complete in the early stages of the reaction. The carbonate

solutions are used almost exclusively in the determination of reducing sugar in biological preparations. The alkalinity is supplied by carbonates or bicarbonates, or their mixtures.

Somogyi [8] and Shaffer and Somogyi [9] studied the copper reduction in mixed carbonate-bicarbonate solutions, particularly with reference to the ratio of carbonate to bicarbonate. They found that the characteristic feature was that when the alkalinity was lower (or the ratio Na_2CO_3:$NaHCO_3$, was lower) the sugar oxidation was slower but that the final amount of copper reduced was higher. The maximum reduction of copper was found to vary inversely with the logarithm of the carbonate : bicarbonate ratio. The rate of reduction conforms roughly with a first-order equation and may be treated as a pseudomonomolecular reaction. The velocity of copper reduction (and of sugar oxidation) is likewise a linear function of the logarithm of the carbonate : bicarbonate ratio and thus presumably of pH.

Shaffer and Somogyi showed that the rate of oxidation varied with the nature of the sugar. With a copper solution having a carbonate : bicarbonate ratio of 1, the rate of reduction diminishes in the order (1) fructose, (2) glucose, (3) galactose, maltose, and arabinose, (4) lactose, and (5) mannose. It is thus necessary to extend the period of heating in the analysis of slowly reacting sugars.

For precise analytical work it is important to prepare the caustic alkali solutions with sodium hydroxide which is free from carbonate. This can be done in a simple manner by preparing a 50-percent solution (by weight) of the sodium hydroxide and allowing it to stand until the carbonate has separated. The solution is then decanted or filtered through asbestos, and a weighed quantity (about 1 g) is titrated against a standard acid. The 50-percent alkali is about 19.3 *N*.

(f) CLARIFICATION OF CRUDE PRODUCTS

Crude natural products and the crude products of the sugar industry require clarification as a preliminary step in the determination of reducing sugars. Basic lead acetate is unsuitable for this purpose, since it precipitates appreciable amounts of reducing sugar. Normal lead acetate, however, while it does not usually produce a filtrate of sufficient brilliancy for polariscopic analysis, meets the requirements of chemical methods of reducing-sugar analysis, for it precipitates colloidal material and aids in the removal of suspensions and material which would otherwise contaminate the precipitated copper. Lane and Eynon [10], in an investigation of its action in the analysis of the products of the cane-sugar industry, found no instance in which it removed reducing substances.

Of even more importance than the removal of the substances mentioned above is the removal of calcium salts. Lane and Eynon have shown that all of the alkaline earths exert an inhibiting effect on the reduction of copper and may cause errors in excess of 5 percent by their retarding action. The deficiency of copper reduced is equally apparent in gravimetric and volumetric methods. An excess of calcium salts renders the end point in the presence of methylene blue indistinct.

In order to remove both lead and calcium salts the filtrate from the lead defecation should be treated either with a 10-percent solution of potassium oxalate or with dry, finely powdered sodium or potassium oxalate. If the former is used, the volume relations must be accurately

observed by diluting to one-tenth greater volume or by some similar procedure. If dry sodium oxalate is used, the original volume of the filtrate is not altered unless large quantities of calcium salts are present.

2. METHODS WHICH REQUIRE FILTRATION OF CUPROUS OXIDE

(a) MUNSON AND WALKER UNIFIED METHOD [11]

This method, which is in more general use in this country than any other gravimetric method is applicable to any sample containing reducing sugars. Tables were prepared by the authors for the more common sugars and sugar mixtures and can be extended to other sugars as the need arises without modification of procedure. Success with this method depends in great measure upon attention to details. If copper or copper oxide is to be weighed, the asbestos must be prepared with care to remove substances soluble in the caustic reagents, and assurance must be had that the precipitate is uncontaminated. If crude substances are under examination, the copper should not be weighed but should be determined analytically. In ordinary practice the simplicity and directness of procedure tend to encourage careless operation, and errors in results are charged against the method. If the concentration of sugar in the sample is subject to control, it is advisable to use the higher ranges of the tables.

(1) Preparation of Soxhlet Reagents.* *Copper sulfate solution.*—Dissolve 34.639 g of pure copper sulfate crystals in water and dilute to 500 ml.

Alkaline tartrate solution.—Dissolve 173 g of Rochelle salt and 50 g of sodium hydroxide in water, and dilute to 500 ml.

(2) Procedure.—Transfer 25 ml each of the copper and alkaline tartrate solutions to a 400-ml Jena or Pyrex beaker, and add 50 ml of reducing-sugar solution, or if a smaller volume of sugar solution is used, add water to make the final volume 100 ml. Heat the beaker upon an asbestos gauze over a Bunsen burner, so regulate the flame that boiling begins in 4 minutes, and continue the boiling for exactly 2 minutes. Keep the beaker covered with a watch glass throughout the entire time of heating. Without diluting, filter the cuprous oxide at once on an asbestos mat in a Gooch crucible, using suction. Wash the cuprous oxide thoroughly with water at a temperature of about 60° C, then with 10 ml of alcohol, and finally with 10 ml of ether. Dry for 30 minutes at 100° C, cool in a desiccator, and weigh as cuprous oxide. If the precipitate is contaminated, determine copper analytically by one of the methods described on page 178. Refer the weight of copper to the Munson and Walker table (table 78, p. 564) to determine the weight of the sugar in the sample.

(b) HAMMOND REDETERMINATION OF THE MUNSON AND WALKER VALUES

In the years that followed the Fehling proposal in 1849 [1] to use an alkaline copper tartrate solution for the quantitative estimation of reducing sugars, many methods were proposed in which various modifications of the concentrations of the components of the Fehling reagent and of the period of boiling the sugar solution and reagent were used. In 1906 Munson and Walker [11] surveyed the various methods and proposed one to unify all the others. This method has deservedly gained widespread use because of its simplicity and ex-

*Commonly known as Fehling's solution.

treme reproducibility of results. Despite the wide utilization of the Munson and Walker table for commercial and scientific purposes, there has been neither a redetermination of their original values nor any needed additions to the scope of the table in 33 years.

Since improved methods for producing pure sucrose and dextrose are easily available, the original Munson and Walker values were redetermined with high precision, and since it is now possible to produce pure levulose by the methods of this Bureau [12] the reducing values of this sugar were also determined.

Within the past few years there has been imported into this country a new type of molasses product made by the partial hydrolysis of raw cane-sugar solution and boiling to a thick sirup. Samples received at this Bureau have a composition varying between 70 to 82 percent total sugar and a reducing-sugar content from 45 to 58 percent. When a sample of this product is taken for analysis to give a total sugar content of 0.4 g in 50 ml of solution, the concentration of reducing sugar is such that the limits of the Munson and Walker table are exceeded. Until the thorough revision and additions to the table were made by Hammond [13] it was necessary to add sucrose to the sample to reduce its invert-sugar content. In order to be able directly to weigh a sample, it was decided to determine data for a new column in the table by using a mixture of invert sugar and sucrose having a total sugar content of 0.3 g.

In redetermining these values, as well as in determining the new ones, the conditions of the Munson-Walker method were rigorously followed and the same concentration of copper reagent was used. However, certain changes in technique were soon found to be necessary. Munson and Walker brought the solution to boiling by heating over a gas flame. This procedure was changed to use electric heating. When the 400-ml beaker was placed in the heater, the 100 ml of solution it contained was entirely surrounded in a nest of the resistance wire. When gas is used to heat such a mixture, a yellow substance often forms on the side of the beaker. This yellow deposit is ordinarily formed when low-grade sugar products, such as blackstrap molasses, are to be analyzed, but has never been observed when the heating is done electrically. The current was controlled by means of a General Radio Corporation Variac and a Raytheon voltage regulator. The solution could readily be brought to boiling in the prescribed 4-minute interval (± 5 sec).

Munson and Walker transferred the precipitated cuprous oxide to Gooch crucibles and weighed the cuprous oxide. This procedure was abandoned and the copper determined electrolytically. The cuprous oxide was transferred to a Gooch crucible, washed, and then dissolved by the slow dropwise addition of 5 ml of 1:1 nitric acid. The copper nitrate was received in a 250-ml beaker; 10 ml of 1:1 nitric acid was added as well as about 5 g of ammonium sulfate. Enough water to cover conveniently the cylindrical gauze electrodes was added, making the total volume of electrolyte about 180 ml. The electrolysis was conducted at a current density of approximately 0.10 amp/dm^2, and, upon completion, the electrolyte was displaced with distilled water before breaking the current. The copper deposit was washed with alcohol, dried 15 minutes at 100° C, cooled in a desiccator, and weighed. All deposits were bright and showed no trace of "burning."

Munson and Walker prepared the invert-sugar solution by hydrolyzing a sucrose solution with 0.02 *N* hydrochloric acid and, upon completion of the hydrolysis, neutralizing with 0.2 *N* sodium hydroxide. In the investigation by Hammond, the invert solution was made by taking equal weights of crystalline dextrose and levulose.

The levulose was prepared by taking a purified sample and dissolving it in water to make a 50-percent solution. Vegetable carbon was added and the solution heated. The filtered solution was evaporated in vacuo to a thick sirup, seeded with pure levulose, and crystallized in motion. The crystals were centrifuged and then washed with absolute alcohol. After drying in the air, the crystals were pulverized, dried for 2 hours at 50° C, and finally dried and stored in a vacuum desiccator. A polariscopic examination showed the levulose to be pure.

The sucrose and dextrose used in this work were Standard Samples 17 and 41, respectively, issued by this Bureau.

The same intervals of concentrations of the sugars employed by Munson and Walker were used, and fresh solutions were made for each determination by weighing the requisite amount of sugar into a sugar scoop, transferring to a 500-ml flask, and completing the volume at 20° C, at which temperature the solution was kept while the aliquots of 50 ml were taken. For the concentration 20 mg per 50 ml, the amounts of sugar necessary for 1 liter of solution were taken. Quadruplicate determinations of each sugar concentration were made.

From the average result of each series of quadruplicate determinations there was calculated by the method of least squares a set of equations for calculating the reducing sugar from any given weight of copper within the limits of the method. In table 78 in the Appendix are shown the reducing-sugar values for each sugar and sugar mixture for values of copper from 10 to 440 mg at intervals of 1 mg. The values for cuprous oxide were computed by multiplying the corresponding value for copper by the factor 1.12585.

Attention is called to the fact that for the columns 0.3 g and 0.4 g of total sugar in table 78, the values are practically identical beyond the concentration of 220 mg. This is probably due to the fact that as the copper content of the copper reagent diminishes during the 2-minute boiling period, the rate of the reaction decreases, so that the differences are of a magnitude approximating the experimental error of the method. A comparison of the copper values of the Munson and Walker table and those of the new table show the Munson-Walker values to be slightly higher for a definite weight of sugar. The differences for dextrose are a few tenths of a milligram, distributed positively and negatively. For invert sugar and the invert-sugar and sucrose mixtures the differences are somewhat larger and, in general, increase with the sugar concentration. It is to be noted that if a comparison is made between a definite weight of copper and the corresponding sugar value, the sugar value in the new table will be higher than that in the Munson and Walker table.

In a critical study of the Munson-Walker method, Jackson and McDonald [35] have shown that cuprous oxide is contaminated with organic decomposition products, even when pure sugars are analyzed, and that the amount of this contamination is almost exactly equal to the difference between Hammond's and Munson and Walker's copper values.

(c) ALLIHN METHOD FOR THE DETERMINATION OF DEXTROSE [14, 15]

Copper sulfate solution.—Dissolve 34.639 g of $CuSO_4.5H_2O$ in water and dilute to 500 ml.

Alkaline tartrate solution.—Dissolve 173 g of Rochelle salt and 125 g of potassium hydroxide in water and dilute to 500 ml.

Description of method.—Place 30 ml of the copper solution, 30 ml of the alkaline tartrate solution, and 60 ml of water in a beaker, and heat to boiling. Add 25 ml of the sugar solution, which must be so prepared as to contain not more than 0.25 g of dextrose, and boil for exactly 2 minutes, keeping the beaker covered. Filter immediately through asbestos without diluting and obtain the weight of copper by one of the methods described on pages 178-185. The corresponding weight of dextrose is found from the Allihn table (table 79, p. 584).

Quisumbing and Thomas found that the maximum amount of copper was reduced at a concentration of caustic alkali of 0.8125 *N*. Soxhlet's copper mixture is 0.625 *N*, whereas Allihn's solution is 0.922 *N* with respect to potassium hydroxide, the calculated normality being referred in each instance to the final reaction mixture containing the sugar. That all three solutions are within the range of high sensitivity is shown by the fact that in spite of varied conditions of analysis they all reduce approximately the same weight of copper. Thus 100 mg of dextrose reduces respectively 201.5, 198, and 195 mg of copper.

(d) QUISUMBING AND THOMAS METHOD

The method of Quisumbing and Thomas [6] was devised after a careful study of the fundamental properties of the reaction had revealed the most favorable conditions for conducting the analysis. In order to obviate the autoreduction of the alkaline copper solution and the reduction of copper by sucrose, and to avoid variations in temperature caused by changes of barometric pressure, the reduction reaction was carried out in a water bath at 80° C. Preliminary experiments had shown that the maximum reduction occurs at an alkalinity of 1.6 *N* and at a ratio of 5 to 6 of sodium hydroxide to 1 of copper. Fifty milliliters of mixed reagent should thus contain 3.2 g of sodium hydroxide and from 0.525 to 0.630 g of copper. With greater concentrations of copper, the total reduction is decreased, while the autoreduction is increased. The concentration of Rochelle salt employed in the Soxhlet reagent was retained.

This method is capable of producing more accurate results than any other gravimetric method. No reduction of copper is caused by sucrose if the sample does not contain more than 400 mg. In its present form the method is limited to materials of low sucrose content. It should be possible, however, to extend the application of the method to samples of high sucrose content by determining the corrections at higher sucrose concentrations. In view of its independence of barometric pressure, the method is useful at high altitudes.

Copper sulfate solution.—Dissolve 41.2 g of $CuSO_4.5H_2O$ and dilute to 500 ml. The crystals should be free from dust or partially dehydrated salt.

Alkaline tartrate solution.—Dissolve 173 g of crystallized Rochelle salt in water in a 500-ml flask, and add the calculated amount of sodium hydroxide solution containing 65 g of sodium hydroxide.

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Fill to a volume of 500 ml. The alkali solution is freed from carbonates in the manner described on page 169.

General procedure.—Measure accurately 25 ml each of the copper sulfate and alkaline tartrate solutions into a 400-ml Pyrex-glass beaker, the diameter of which is about 9 cm. Add 50 ml of sugar solution containing 50 to 150 mg of dextrose, levulose, or invert sugar; or 100 to 300 mg of lactose or maltose. Cover the beaker with a watch glass, and place the beaker in a water bath maintained at 80° C. After digesting for exactly 30 minutes, filter the cuprous oxide by suction through a mat of asbestos in a Gooch crucible. Wash the precipitate in the usual manner and determine the copper by one of the methods described on page 178.

From the weight of copper or cuprous oxide obtained, find the corresponding weight of reducing sugar from table 80, p. 586.

(e) BERTRAND METHOD

This method [16] has been but little used in the United States. It is more widely employed in Europe, more frequently in the pure chemistry of carbohydrates than in commercial analysis.

The reagents are prepared as follows:

(a) 40 g of pure $CuSO_4.5H_2O$ dissolved to 1 liter.

(b) 200 g of Rochelle salt and 150 g of sodium hydroxide dissolved to 1 liter.

Into a 150-ml Erlenmeyer flask transfer 20 ml each of solutions (a) and (b) and 20 ml of the sugar solution, which should contain not more than 100 mg of reducing sugars. Heat to boiling and keep at gentle ebullition for exactly 3 minutes. Filter through asbestos and determine the reduced copper as follows by Mohr's volumetric permanganate titration. Reference table 81 is given on page 587. Transfer the asbestos film to the beaker, add about 30 ml of hot water, and heat the precipitate and asbestos thoroughly. Rinse the crucible with 50 ml of a hot saturated solution of ferric sulfate in 20-percent sulfuric acid, receiving the rinsings in the beaker containing the precipitate. After the cuprous oxide is dissolved, wash the solution into a large Erlenmeyer flask, and immediately titrate with a standard solution of potassium permanganate. One milliliter of the permanganate solution (0.1573 N) should equal 0.010 g of copper. Standardize the permanganate against pure sodium oxalate.

(f) HERZFELD METHOD FOR DETERMINATION OF LESS THAN 1.5 PERCENT OF INVERT SUGAR IN SUCROSE

Many of the products of the cane- and beet-sugar industries, particularly in the later stages of the processes, contain small residual quantities of invert sugar which cannot be accurately determined by the Meissl and Hiller method. The Herzfeld method [17] is designed to apply to this range of concentrations. It therefore serves to supplement the Meissl and Hiller method (p. 175), which is serviceable at ratios of invert sugar to sucrose greater than 1½ percent. In his fundamental research, Herzfeld determined the copper reduced by a 10-g sample of total sugar containing varying quantities of added invert sugar, collecting the precipitated copper in a thick-walled filter tube (12 by 2 cm) containing 1.5 cm of asbestos supported by a platinum cone. The cuprous oxide was burned at low heat to cupric

oxide in order to destroy precipitated organic matter and then reduced to copper in a stream of hydrogen. Herzfeld's procedure, in spite of its early date, thus corresponds to modern procedure. He made triplicate or quadruplicate determinations at seven ratios of invert sugar to sucrose and plotted a smooth curve through the determined points.

The method is well adapted to the determination of reducing sugar in the higher grades of commercial raw sugar. These in general require a preliminary clarification with normal lead acetate. This can be conveniently done by weighing out a 20-g sample, transferring to a 100-ml flask, adding normal lead acetate, making to volume, and filtering. To the filtrate, dust in sufficient dry sodium oxalate to precipitate the excess lead and filter. A volume of 50 ml of the filtrate will contain 10 g of the original sample.

An alternative method [18] is to dissolve 44 g of the sample and transfer to a 200-ml volumetric flask. Clarify with normal lead acetate, make to volume, and filter. Measure 100 ml of the filtrate into a 100- to 110-ml flask, add sufficient sodium sulfate to precipitate the excess lead, and filter. Take for analysis 50 ml of the filtrate.

Add the 50-ml solution thus prepared to 50 ml of mixed Soxhlet solution and heat rapidly to boiling. From the moment when the boiling becomes vigorous continue the boiling for exactly 2 minutes. Then add 100 ml of cold water freed from air by previous boiling and collect the precipitated copper by filtration and thorough washing. Determine the copper by any of the usual methods (p. 178). Refer the weight of copper to table 82.

It was recognized by Herzfeld that the influence of sucrose upon the amount of copper reduced was relatively considerable and variable. Much of the variability was ascribed to the variable degree of superheating of the sugar solution during the period of boiling. Vondrak [19] in a careful study showed that the boiling temperature of the reaction mixture rose to 104° to 105° C, but the addition of talcum or roughened glass beads diminished the boiling temperature to 102° C and, moreover, the analytical results were far more reliable than those obtained by the original method. He sought to improve the procedure by using glass beads, 5 to 6 mm in diameter, which had been roughened by vigorous shaking in a stout bottle for 10 minutes with 2 percent of coarse carborundum (No. 100). These beads can be used repeatedly if after each use they are again shaken with carborundum for 5 minutes.

The analysis is conducted as prescribed by Herzfeld, with the exception that five roughened glass beads are added to the reaction mixture. The reducing action of sucrose is diminished and consequently a revision of Herzfeld's table (table 83, p. 589) was required. Interpolation between adjacent values of copper yields accurate results.

(g) MEISSL AND HILLER METHOD FOR DETERMINING INVERT SUGAR ADMIXED WITH SUCROSE IN ALL PROPORTIONS

At a very early period Meissl recognized the importance of correcting the precipitated copper for the reducing action of sucrose. Meissl and Wein determined the reducing powers of mixtures containing less than 10 percent of invert sugar. In order to extend the applicability of the principle, Hiller [20] determined the reducing action of invert sugar in the presence of widely varying quantities of sucrose and con-

structed a table of factors by which the weight of copper should be multiplied in order to yield invert sugar correctly in the presence of all ratios of sucrose to invert sugar up to 99 percent. Hiller's table of factors (p. 589) illustrates well the effect of sucrose. Each column gives the factors (expressed in percent) for a constant weight of invert sugar in the presence of varying quantities of sucrose. In extreme cases an error of nearly 30 percent could be introduced by disregarding the effect of sucrose.

In order to select the proper factor, it is necessary to determine polariscopically the approximate sucrose content of the sample. The direct polarization in the presence of invert sugar is not a correct measure of sucrose but is sufficiently exact for the purpose, except in very low-grade products. If the sucrose is determined by the Clerget method, its percentage should be substituted for P, the direct polarization, in the formulas given below.

The Hiller factors were carefully determined, but not with the rigid specifications which are imposed at the present time. He used Fehling solution, boiled "2 to 3 minutes," and collected the precipitate on a paper filter, ignited, and reduced the oxide by hydrogen to copper. It is not essential that enough solution be taken to precipitate nearly all of the copper, but, in general, the results are more accurate at higher than at lower sugar concentrations.

Prepare a solution of suitable concentration of the material to be examined, clarify with neutral lead acetate, and remove the excess of lead with an alkali oxalate or sodium phosphate. Prepare a series of solutions in large test tubes by adding 1, 2, 3, 4, and 5 ml of this solution to each tube successively. Add 5 ml of mixed Soxhlet reagent to each, heat to boiling, boil 2 minutes, and filter. Note the volume of sugar solution that gives the filtrate lightest in tint but still distinctly blue. Place 20 times this volume of the sugar solution in a 100-ml flask, dilute to the mark, and mix well.

Transfer 50 ml of mixed Soxhlet reagent and 50 ml of the solution to a 250-ml beaker. Heat this mixture at such a rate that a period of approximately 4 minutes is required to bring it to the boiling point, and then boil for exactly 2 minutes. Add 100 ml of cold recently boiled water. Filter immediately through asbestos, and determine the copper by one of the methods described on page 178.

Let

Cu = the weight of copper obtained,

P = polarization of the sample (or sucrose by Clerget analysis),

W = the weight of the sample in the 50 ml of solution used for the determination,

F = the factor obtained from Hiller's table.

Then

$$\frac{Cu}{2} = Z, \text{ approximate weight of invert sugar,}$$

$$Z \times \frac{100}{W} = Y, \text{ approximate percentage of invert sugar,}$$

$$\frac{100P}{P+Y} = R, \text{ approximate percentage of sucrose in mixture of sugars,}$$

$$100 - R = I, \text{ approximate percentage of invert sugar,}$$

$$\frac{Cu\,F}{W} = \text{percentage of invert sugar.}$$

The factor, F, for calculating copper to invert sugar, is found in table 84.

Example: The polarization of a sugar is 86.4, and 50 ml of solution containing 3.256 g of sample gave 0.290 g of copper.

$$\frac{Cu}{2}=\frac{0.290}{2}=0.145=Z.$$

$$\frac{Z\times 100}{W}=0.145\times\frac{100}{3.256}=4.45=Y.$$

$$\frac{100P}{P+Y}=\frac{8640}{86.4+4.45}=95.1=R.$$

$$100-R=100-95.1=4.9=I.$$

$$R:I=95.1:4.9.$$

By consulting the table, it will be seen that the vertical column headed 150 is nearest to Z, 145, and the horizontal column headed 95:5 is nearest to the ratio of R to I, 95.1:4.9. Where these columns meet there is found the factor 51.2, which enters into the final calculation:

$$\frac{Cu\,F}{W}=\frac{0.290\times 51.2}{3.256}=4.56 \text{ percent of invert sugar.}$$

(h) BROWN, MORRIS, AND MILLAR METHOD FOR REDUCING SUGAR IN MOLASSES [21]

The general method of these authors has been adapted by W. A. Davis to the determination of reducing sugar in cane and beet molasses. The method is extensively used in Great Britain. It is applied to solutions containing 1 g of molasses in 100 ml (not defecated). The Fehling solutions contain 34.639 g of copper sulfate crystals in 500 ml, and 173 g of Rochelle salt and 65 g of sodium hydroxide in 500 ml, respectively. Mix 25 ml of each of the two solutions in a 250-ml beaker of tall lipped form and heat in a gently boiling water bath for 6 minutes. Add 50 ml of the molasses solution (1 g in 100 ml), cover the beaker, and continue the heating for 12 additional minutes. Collect the cuprous oxide in a Gooch crucible, wash with 200 ml of boiling water, and finally with alcohol. Dry and oxidize to copper oxide by placing the Gooch crucible in a larger ordinary crucible in a tilted position, heat gently at first, and finally strongly over a Tecla burner (but not with a blast lamp). Correct the weight of copper oxide for the quantity (usually less than 1 mg) obtained in a blank determination.

For weights of copper oxide less than 0.245 g multiply the weight of copper oxide by the factor 81.5 to obtain directly the percentage of invert sugar in the sample. For weights greater than 0.245 g, use the factors given in table 20.

TABLE 20.—*Factors for calculating invert sugar from copper oxide*

Copper oxide	Factor	Copper oxide	Factor
g		*g*	
0.2430	82.31	0.3546	84.60
.2668	82.46	.3764	85.02
.2898	82.82	.3971	85.62
.3121	83.31	.4177	86.19
.3339	83.86	.4376	86.84

3. DETERMINATION OF COPPER

(a) GENERAL

The estimation of copper in the cuprous oxide precipitate may be accomplished gravimetrically or volumetrically. The gravimetric methods, which consist in the weighing of the cuprous-oxide precipitate either directly or after conversion to copper or cupric oxide, may be employed only in case the precipitate is uncontaminated. Contamination may be caused by the precipitation or inclusion of inorganic or organic impurities in the sample. Such precipitation is more likely to occur when cruder samples are analyzed.

Sherwood and Wiley [22] made an extended series of analyses of pure and crude products, which, in table 21, is condensed by computing the averages. Included in the table is the mean of a number of analyses made by Hammond.

TABLE 21.—*Comparison of methods for determining reduced copper*

Material	Author	Reduced copper				
		From weight of Cu_2O	From weight of CuO	Iodometric	Reduced by alcohol	Electrolytic
		g	*g*	*g*	*g*	*g*
Molasses residuum	Sherwood and Wiley	0.3176	0.3023	0.2988		
Corn juice	do	.3360		.3134		
Malt extract	do	.2858		.2638		
Beer	do	.0750		.0750		
Molasses	do	.4628		.4520		
Pure dextrose	do	.2773		.2773		
Molasses	Hammond				0.2519	0.2467
Pure dextrose	do	.3791			.3780	.3784

The data presented indicate that the iodometric and electrolytic methods yield the true weights of reduced copper. It is evident at once that other methods yield correct results only with relatively pure substances. Unfortunately, the materials selected for illustration are extremely crude products and do not permit judgment as to what classes of materials can safely be analyzed gravimetrically. Unquestionably there are many classes of commercial products sufficiently free from impurities which may contaminate the copper precipitate, but the analyst must exercise discretion in the selection of a method of copper analysis. Inasmuch as some of the volumetric methods are less time-consuming than the gravimetric methods, the recommendation appears justified that each analyst select one which best meets his requirements, leaving the gravimetric methods for materials of unquestionable purity. The data in table 21 show that the error of analysis due to contamination is greatly diminished by ignition to cupric oxide, which is weighed directly or reduced to copper. Inorganic contamination is not removed by this procedure.

(b) GRAVIMETRIC METHODS

Preparation of asbestos [11].—Digest the asbestos, which should be of the amphibole variety, with hydrochloric acid (1+3) for 2 to 3 days. Wash free of acid, digest for a similar period with 10-percent sodium hydroxide solution, and then treat for a few hours with hot

alkaline tartrate solution (old alkaline tartrate solutions are suitable) of the strength used in sugar determinations. Wash the asbestos free from alkali, digest for several hours with nitric acid (1+3), and after washing free from acid, shake with water into a fine pulp. In preparing the Gooch crucible, make a film of asbestos ¼-inch thick and wash thoroughly with water to remove fine particles of asbestos. If the precipitated cuprous oxide is to be weighed as such, wash the crucible with 10 ml of alcohol, then with 10 ml of ether, dry for 30 minutes at 100° C, cool in a desiccator, and weigh. For the most careful work, the analyst should assure himself that the weight of the crucible remains constant, by pouring 100 ml of clear hot alkaline solution through it, washing, drying, and reweighing.

A more rapid and perhaps equally effective method developed by Brewster and Phelps for the preparation of asbestos is described on page 324.

Determination.—The gravimetric estimation of copper by direct weighing of cuprous oxide has been described in detail on page 170. To eliminate organic contamination of the copper precipitate, it may be converted to cupric oxide. Ignite at red heat for 15 to 20 minutes, preferably in a muffle or in such a manner as to avoid exposure of the precipitate to hot reducing gases. Too intense heating must be avoided. Cool in a desiccator and weigh rapidly, since cupric oxide is hygroscopic. Multiply the weight of cupric oxide by 0.7989 to obtain the weight of copper. For the most careful work the crucible containing the asbestos should be heated previous to the filtration in order to insure its constancy of weight during the analysis.

Because of the hygroscopic nature of cupric oxide, and to eliminate the possible error arising from its incomplete oxidation, it is sometimes advisable to reduce the precipitate to metallic copper. This can be effected readily by exposing the precipitate to a continuous stream of hydrogen and at the same time heating gently with a Bunsen flame until reduction is complete. Cool in a stream of hydrogen. This method is facilitated by use of a filtering tube constructed of hard glass, the asbestos being supported by a perforated disk or platinum cone. This tube permits the direct application of the flame during reduction, whereas the Gooch crucibles must be supported in a suitable glass chamber.

A convenient method of reduction to copper is in use by the United States Customs Service (Treasury Decision 39350; 1922). The method was devised in principle by Wedderburn [23].

Wash the cuprous oxide thoroughly with water at a temperature of about 60° C, then with 10 ml of alcohol, and dry for 30 minutes in a water oven at 100° C. Heat the crucible for 30 minutes over a Bunsen burner. The precipitate is reduced to metallic copper in methyl-alcohol vapors. This is done by placing about 100 ml of methyl alcohol in a 400-ml beaker, and placing a triangular support in the beaker so that the crucible is above the level of the alcohol. Heat the covered beaker on a hot plate to boiling, remove the cover, and place the hot Gooch crucible on the triangle. This ignites the alcohol vapors. Immediately cover the beaker with a watch glass and allow the Gooch to remain for about 3 minutes, remove, cool in a desiccator, and weigh.

(c) ELECTROLYTIC DEPOSITION FROM NITRIC ACID SOLUTION [24]

Upon completion of the copper reduction reaction, decant the hot solution through an asbestos mat in a Gooch crucible and wash the beaker and precipitate thoroughly with hot water. Transfer the asbestos mat from the crucible to the beaker with a glass rod and rinse the crucible with 14 ml of nitric acid (1+1), allowing the rinsings to flow into the beaker. After the cuprous oxide is dissolved, dilute to 100 ml, heat to boiling, and continue the boiling for about 5 minutes to remove the oxides of nitrogen. Cool, filter, and dilute to 200 ml. Add 1 drop of 0.1 *N* hydrochloric acid and mix thoroughly.

If extreme care is exercised to avoid spattering, the cuprous oxide can be dissolved by allowing the nitric acid to flow down the walls of the crucible. Keep the crucible covered as well as possible with a small watch glass. Collect the filtrate in a 250-ml beaker and wash the watch glass and the tip of the pipette with a jet of water. Continue as described above, beginning with "heat to boiling."

For electrolysis use cylindrical electrodes of platinum gauze 1.5 and 2 inches, respectively, in diameter, and 1.75 inches in height, thoroughly cleaned, ignited, cooled in a desiccator, and weighed. Insert the electrodes in the copper solution so that the surface of the cathode clears the anode by at least 5 mm and both electrodes almost touch the bottom of the beaker. Electrolyze with a current of 0.2 to 0.4 ampere until deposition is complete, usually overnight. Without interrupting the current, slowly lower the beaker and at the same time wash the electrodes with a stream of distilled water. Immediately immerse the electrodes in another beaker of water, lower the beaker, and break the current. Rinse the cathode with ethyl alcohol and dry for a few minutes in an oven at 110° C. Cool in a desiccator and weigh.

(d) THIOSULFATE METHOD

When potassium iodide is added to a cupric copper solution, cuprous iodide is precipitated and iodine liberated according to the equation

$$Cu^{++}+2I^{-}\rightleftharpoons Cu^{+}+I^{-}+1/2\ I_2.$$

The reaction is reversible and has been shown by Bray and MacKay [25] to obey the mass law within certain limits in dilute solutions. For the purposes of titration the reversible reaction can be made to run to completion in either direction by adjustment of conditions. Thus by the removal of cupric ions in the form of a complex ion or by great dilution the reaction can be made to run quantitatively from right to left, while the presence of a large excess of iodide ions, together with the removal of cuprous ions in the form of insoluble cuprous iodide, causes the reaction to run quantitatively from left to right.

Shaffer and Hartmann [26] determined the positions of the equilibria and concluded that for the determination of cupric salts potassium iodide must be added to give a final concentration of about 0.25 *M* (4 to 5 g per 100 ml of solution). For the determination of cuprous salts, the solution must be so diluted that the final concentration of copper and of iodide does not exceed about 0.005 *M* each. Equivalent to this dilution, which curtails the general usefulness of the method, is the addition of potassium oxalate, which forms anions containing both copper and oxalate. The cuprous titration can thus be made conveniently without excessive dilution.

The principles established by Shaffer and Hartmann are the basis of the cupric titration given in detail below. The cuprous titration is generally made directly in the reaction mixture, and examples are given in several of the special reducing-sugar methods described under "volumetric processes" page 185. (See also Methods of Analysis of AOAC [27].)

Reagent.—Standard thiosulfate solution.—Prepare a solution containing 39 g of pure $Na_2S_2O_3.5HO_2$ in 1 liter. Weigh accurately 0.2 to 0.4 g of pure Cu and transfer to a 250-ml Erlenmeyer flask roughly graduated by marks at 20-ml intervals. Dissolve the Cu in 5 ml of a mixture of equal volumes of HNO_3 and H_2O, dilute to 20 or 30 ml, boil to expel the red fumes, add a slight excess of strong Br water, and boil until the Br is completely driven off. Cool, and add NaOH solution with agitation until a faint turbidity of $Cu(OH)_2$ appears (about 7 ml of a 25-percent solution is required). Discharge the turbidity with a few drops of acetic acid and add 2 drops in excess.

Prepare a solution of 42 g of KI in 100 ml of solution made very slightly alkaline to prevent formation of HI and its oxidation.

It is essential for the thiosulfate titration that the concentration of KI in the solution be carefully regulated. If the solution contains less than 320 mg of Cu, 4.2 to 5 g of potassium iodode should have been added at the completion of the titration for each 100 ml of total solution. If greater quantities of Cu are present, the amount of KI should be proportionately greater. The KI solution should be added slowly from a burette, with constant agitation.

Observe the volume of the Cu solution and add 1 ml of KI solution for each 10 ml of the solution undergoing titration. Titrate at once with the thiosulfate solution until the brown color becomes faint. Again observe the volume and add an additional volume of KI to make the required concentration, noting from the volume of the thiosulfate the approximate Cu content of the solution. Add sufficient starch indicator to produce a marked blue coloration. Continue the titration cautiously until the color changes toward the end to a faint lilac. As the end point is approached, add the thiosulfate in fractions of drops, allowing the precipitate to settle slightly after each addition. One ml of thiosulfate solution equals about 10 mg of Cu.

Determination.—Wash the precipitated Cu_2O, cover the Gooch crucible with a watch glass, and dissolve the oxide by means of 5 ml of $HNO_3(1+1)$ directed under the watch glass with a pipette. Collect the filtrate in a 250-ml Erlenmeyer flask roughly graduated by marks at 20-ml intervals, and wash the watch glass and Gooch crucible free from Cu. Proceed as directed under "Reagent," beginning with "boil to expel the red fumes."

Foote and Vance [28] have studied the titration and have proposed that an addition of 2 g of ammonium thiocyanate be made when the tiration has proceeded nearly to the end point. In the usual procedure the cuprous iodide is not white but slightly discolored, apparently as a result of the adsorption of iodine. Because of the greater insolubility of cuprous thiocyanate, the surface particles of cuprous iodide are changed to thiocyanate, releasing the adsorbed iodine, which thus consumes a slight additional volume of thiosulfate. The end point is exceedingly sharp, the precipitate turning completely white. This modification can be introduced into the procedure described above,

provided both standardization and determination are conducted in the same manner.

Foote and Vance performed the titration in the presence of 5 ml of sulfuric acid and in the presence of the same reagent buffered by 3 g of ammonium acetate and obtained the same analytical results. Even a small volume of nitric acid (1 ml) produced no measurable deviation. In view of these results, it is probable that the procedure given on page 181 could be materially simplified.

(e) PERMANGANATE METHOD

When cuprous oxide is dissolved in a ferric sulfate solution the latter is reduced to ferrous sulfate and can be titrated with standard permanganate. The reduced copper can then be computed on the basis of the stoichiometric relations. This method of determination of reduced copper was originally proposed by Mohr [29], but has erroneously been attributed to Bertrand [16]. Mohr prescribed that the ferric sulfate be dissolved in sulfuric acid, and this procedure was adopted by Bertrand, who based his tables (see page 587) upon the volume of permanganate consumed, instead of referring his sugar to copper. Subsequently, it was discovered that the permanganate volumes, when converted to copper, gave results which were invariably about 1.4 percent too low, and many authors advocated a blanket correction by this amount. Schoorl and Regenbogen [30] ascribed the low results to the rapid oxidation of ferrous sulfate by air. The oxidation is more rapid than is ordinarily the case with ferrous sulfate, but in the presence of copper, which increases the rate of oxidation, and in the presence of the asbestos, which carries finely subdivided air, the amount of oxidation appears to be accounted for.

Schoorl and Regenbogen found that if the cuprous oxide was dissolved in neutral ferric sulfate, or better, ferric alum, before addition of sulfuric acid, correct results were obtained. A brownish-red clear solution is obtained in which the Fe_2O_3 apparently remains dissolved in the form of a basic salt. The authors suggest that the following reaction occurs:

$$Cu_2O+2Fe_2(SO_4)_3 \rightarrow 2CuSO_4+2FeSO_4+Fe_2O_3+SO_3.$$

Reagents.—Prepare a potassium permanganate solution, about 0.1573 *N*, containing 4.98 g per liter. After several days' aging, filter through asbestos or sintered glass. Standardize by either of the following methods.

(a) Transfer 0.35 g of sodium oxalate (dried at 103°C) [31] to a 600-ml beaker. Add 250 ml of sulfuric acid (5+95) previously boiled for 10 minutes and cooled to 27±3°C. Stir until the oxalate is dissolved. Add 29 to 30 ml of permanganate solution at a rate of 25 to 35 ml per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds). Heat to 55° to 60°C, and complete the titration by adding permanangate solution until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml dropwise, allowing each drop to become decolorized before the next is added. Determine the excess of solution (usually 0.03 to 0.05 ml) required to impart a pink color to the same volume of acid boiled and cooled to 55° to 60°C.

In potentiometric titrations the correction is negligible if the end point is approached slowly.

(b) Transfer [32] about 0.3 g of As_2O_3 (dried at 110°C) to a 400-ml beaker. Add 10 ml of a cool solution of sodium hydroxide (20 percent) and allow to stand until dissolved, stirring occasionally. Add 100 ml of water, 10 ml of HCl (sp gr 1.18), and 1 drop of 0.0025 *M* KIO_3 or KI. Titrate with permanangate solution until a faint pink color persists for 30 seconds, adding dropwise the last 1 to 1.5 ml, and allowing each drop to become decolorized before adding the next. Determine by a blank test with all reagents except As_2O_3, the volume of $KMnO_4$ (usually about 0.03 ml) required to duplicate the pink color of the end point. The end point can also be determined with ferrous phenanthroline indicator, in which case 1 drop of a 0.025 *M* solution of the indicator is added as the end point is approached. Determine blank correction.

The titration can also be conducted potentiometrically.

Ferric sulfate.—Dissolve 135 g of ferric ammonium alum or 55 g of $Fe_2(SO_4)_3$ (anhydrous) and dilute to 1 liter. Determine $Fe_2(SO_4)_3$ in the stock supply by strong ignition to Fe_2O_3. Ferric sulfate, particularly after exposure to light, contains a small quantity of reducing substance which must be oxidized before the solution is used. Titrate 50 ml of the ferric sulfate solution, acidified with 20 ml of 4 *N* sulfuric acid, with the permanganate and use the titer as a zero-point correction in subsequent titrations.

4 N sulfuric acid.

Ferrous phenanthroline indicator.—Dissolve 0.7425 g of orthophenanthroline monohydrate in 25 ml of 0.025 *M* ferric sulfate solution (6.95 g of $FeSO_4.7H_2O$ in 1 liter).

Procedure.—Filter the cuprous oxide in a Gooch crucible and wash the beaker and precipitate thoroughly. Transfer the asbestos film to the beaker with the aid of a glass rod. Add 50 ml of the ferric sulfate solution and stir vigorously until the cuprous oxide is completely dissolved. Examine for complete solution, holding the beaker above the level of the eye. Add 20 ml of 4 *N* sulfuric acid and titrate with standard permanganate. As the end point is approached, add 1 drop of ferrous phenathroline indicator. At the end point the brownish solution changes to green. One milliliter of 0.1573 *N* permanganate equals 10 mg of copper.

The concentration of the permanganate solution in the method described above is such that a single filling of the burette supplies enough reagent for the determination of the maximum amount of copper precipitated by any of the usual methods of analysis. For many purposes the reagent is too concentrated. Thus, for the small quantities of copper precipitated by high-grade cane- or beet-sugar samples, a *N*/30 permanganate solution is more commonly used. An outstanding disadvantage of the method is that the larger weights of cuprous oxide dissolve with great difficulty in the ferric sulfate solution.

(f) DICHROMATE METHODS

(1) Electrometric.—Jackson and Mathews [33] have described a rapid and convenient method for the determination of reduced copper, in which cuprous oxide is oxidized in hydrochloric acid solution by an excess of standard dichromate, the excess being determined by back titration with ferrous sulfate to an electrometric end point. The electrometric apparatus can be obtained by purchase or it may be

assembled easily. Its arrangement is shown diagrammatically in figure 38. The current from two dry cells, E, flows continuously through a resistance, *R*, of about 3,000 ohms. The potassium chloride bridge, *C*, of a calomel cell and a bare platinum wire, *P*, dip into the solution undergoing analysis. The sliding contact on the rheostat is so adjusted as to produce a zero reading on the galvanometer, *G*, when the electrodes dip into an acidified ferrous-ferric system containing a slight excess of dichromate. As ferrous sulfate is added, there is but slight change in the position of the galvanometer needle until the end point is reached. At the end point the deflection of the needle is so large that no actual measurements of electromotive force are required. The galvanometer must be fairly sensitive.

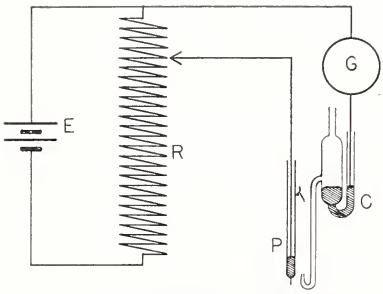

FIGURE 38.—*Apparatus for electrometric determination of copper.*

Reagents.—Potassium dichromate.—Dissolve 7.7135 g of pure crystals, preferably pulverized and dried at 150° C, and make to a volume of 1 liter. One milliliter of this solution, which is 0.1573 *N*, is equivalent to 10.00 mg of copper.

Ferrous ammonium sulfate.—Dissolve 61.8 g of the hexahydrate crystals, add 5 ml of sulfuric acid, and make up to 1 liter. Equally suitable is 43.8 g of $FeSO_4.7H_2O$, acidified and made to 1 liter. The ferrous solutions are oxidized slowly by air and must occasionally be titrated against the standard dichromate solution.

Procedure.—Collect the precipitated cuprous oxide on a Gooch crucible and wash thoroughly. Detach the mat with a glass rod and transfer to the reaction beaker. Add a small volume of water and disintegrate the mat. Pipette accurately a volume of standard dichromate in excess of the quantity required to oxidize the cuprous oxide. In general, the approximate weight of copper will be known or can be roughly estimated, but in any case a sufficient volume must be added to supply an assured excess. Add from a graduated cylinder 50 ml of 1+1 hydrochloric acid with stirring, and continue to stir until all cuprous oxide is dissolved. Immerse the crucible in the solution and be sure that the adhering cuprous oxide is dissolved. Remove the crucible with the glass rod, washing it free of solution. Dilute the solution to about 250 ml and titrate the excess dichromate with ferrous sulfate to an electrometric end point. Determine the ratio of ferrous sulfate to dichromate, and thence compute the volume of dichromate required for the oxidation of cuprous oxide. This volume multiplied by 10 gives directly the number of milligrams of copper reduced.

(2) COLORIMETRIC.—Many laboratories lack the necessary equipment for electrometric titration, but a number of suitable internal indicators are known which make possible a colorimetric end point. A particularly serviceable one, orthophenanthroline,[10] was shown by Walden, Hammett, and Chapman [34] to be applicable in oxidation-reduction reactions.

Jackson and McDonald [35] have applied the colorimetric dichromate method of titration to the determination of copper in cuprous oxide.

[10] Manufactured by the G. Frederick Smith Chemical Co., Columbus, Ohio.

Reagents.—Potassium dichromate.—Standard solution, 0.1573 *N*, containing 7.7135 g of pure dry crystals in 1 liter. One milliliter is equivalent to 10 mg of copper. *Ferrous ammonium sulfate.*—Dissolve 61.9 g of the hexahydrate, add 5 ml of sulfuric acid, and complete the volume to 1 liter. *Hydrochloric acid.*—Approximately 6 *N*. *Phenanthroline-ferrous complex.*—Dissolve 0.725 g of orthophenanthroline monohydrate in 25 ml of 0.025*M ferrous sulfate solution* (6.95 g of $FeSO_4.7H_2O$ in 1 liter).

Procedure.—Estimate the volumes of hydrochloric acid and water which at the end of the titration will yield a concentration of HCl of about 2 *N* in about 200 ml of final volume. An error of from 5 to 10 percent can be tolerated.

Collect the precipitated cuprous oxide on a Gooch crucible and wash thoroughly. Detach the mat with a glass rod and transfer to the reaction beaker. Add a small volume of water and disintegrate the mat. Pipette accurately a volume of standard dichromate in excess of the quantity required to oxidize the cuprous oxide. In general, the approximate weight of copper will be known or can be roughly estimated, but in any case a sufficient volume must be added to supply an assured excess. Add rapidly the whole required volume of hydrochloric acid with continuous stirring and continue to stir until all cuprous oxide is dissolved. Immerse the crucible in the solution and be assured that the adhering cuprous oxide is dissolved. Remove the crucible with the glass rod and wash it with the water from the graduate. Add 1 drop of phenanthroline solution and titrate with ferrous sulfate to the permanent appearance of the brown ferrous-phenanthroline complex. As the end point is approached, the brown color appears and fades as each of the last few drops is added. The ferrous sulfate must be added until the color is permanent, the additions finally being in fractions of drops.

Determine the ratio of concentrations of ferrous sulfate and dichromate and then compute the volume of dichromate required for the oxidation of cuprous oxide. This volume multiplied by 10 gives directly the number of milligrams of copper reduced.

The electrometric and colorimetric dichromate methods described above are still in an experimental stage in the laboratories of this Bureau. A comparison has been made of the values of copper reduced by the Munson and Walker method and determined by the thiosulfate and by colorimetric dichromate titration, respectively. At low concentrations of copper, identical values were obtained by the two methods. Above 200 mg of copper, systematic differences occurred, which rose to a maximum of 0.2 percent for levulose and 0.3 percent for invert sugar. This discrepancy would disappear if a special table were used for the dichromate methods. Further studies are in progress, since the methods recommend themselves on account of their great rapidity and convenience.

4. VOLUMETRIC METHODS

(a) LANE AND EYNON METHOD

The most convenient, most expeditious, and frequently the most accurate method for the determination of reducing sugars is the volumetric method of Lane and Eynon [36]. In principle, the method involves the determination of the volume of sugar solution required

to reduce completely a measured volume of alkaline copper solution, the end point being internally indicated by the reduction of methylene blue to methylene white by a minute excess of reducing sugar. Methylene blue is a thiazine dye, intensely colored and of oxidation reduction potential well suited to the titration of reducing sugars. A few drops of a 1-percent solution of this dye impart an intense blue color to the reaction mixture, which, in the absence of air, is almost instantly reduced to the leuco base by an excess of reducing sugar. The methylene white is rapidly reoxidized by air, particularly at the high alkalinity of the reaction mixture. Hence it is essential that air be excluded during the titration. This is accomplished by causing an uninterrupted current of steam to issue from the neck of the flask in which the analysis is performed.

Lane and Eynon determined the weight of each sugar required to reduce the copper completely. These weights, which vary with the nature of the sugar and with its concentration, constitute a table of factors (tables 85 and 86), from which the proper one may be selected when the titer is known. The concentration of sugars is then

$$\frac{\text{Factor}\times 100}{\text{Titer}}=\text{mg of sugar in 100 ml.}$$

(1) Standard Method of Titration.—Ten or twenty-five milliliters of mixed Soxhlet reagent is measured into a flask of 300- to 400-ml capacity, and treated cold with almost the whole of the sugar solution required to effect reduction of all the copper, so that if possible not more than 1 ml is required later to complete the titration. The approximate volume of the sugar solutions required is ascertained by a preliminary incremental titration. The flask containing the cold mixture is heated over an asbestos-gauze plate. After the liquid has begun to boil, it is kept in moderate ebullition for 2 minutes, and then, without removal of the flame, 3 to 5 drops of the methylene blue indicator are added, and the titration is completed in 1 additional minute, so that the reaction liquid boils altogether for about 3 minutes without interruption.

The visual end point coincides with the disappearance of cupric ions and hence is the same as that marked by the ferrocyanide and the electrometric test. It has the advantage over the ferrocyanide test that the search for the end point can be completed without interruption of the titration.

Like all volumetric reducing-sugar methods, this method produces best results if almost all the sugar required is added in the early stages of the analysis. Usually the sugar concentration is not known with sufficient certainty to do this. Consequently, Lane and Eynon advise performing a preliminary titration in order to determine the approximate volume of solution required. This is most conveniently accomplished by adding an initial volume of 15 ml of the sugar solution to the measured volume of copper solution, boiling for about 15 to 20 seconds, and then adding further increments of sugar until the blue color of the copper solution has nearly disappeared. This point can be fairly judged within 1 or 2 ml of sugar solution. At this point the methylene blue is added and the titration completed dropwise, the period of operation occupying as nearly 3 minutes as possible.

In the analysis of solutions of the hexoses, this incremental method is nearly as reliable as the standard method, but with solutions of the disaccharides and solutions containing sucrose, it is desirable to repeat the titration by the standard method.

The outlet of the burette should be fitted with a rubber tube connected with a glass tube bent twice at right angles in order that the solution shall not be heated by the reaction mixture. Glass stopcocks cannot be used as they invariably jam under the fluctuating temperature conditions.

Soxhlet's modification of Fehling's solution is used for the method. The solution is made by mixing exactly equal volumes of (1) a copper sulfate solution containing 69.28 g of $CuSO_4.5H_2O$ per liter, (2) a solution containing 346 g of Rochelle salt and 100 g of sodium hydroxide per liter.

Pure copper sulfate ordinarily contains somewhat more than the theoretical amount of water. Hence the authors recommend that a standardization of the solution be performed by titration against a standard invert-sugar solution and that any small adjustment of the copper solution be made to correspond with the tables by addition of copper sulfate or water. Twenty-five milliliters of solution (1) should contain 440.9 mg of copper.

The standard solution of invert sugar may be prepared as follows: A solution of 9.5 g of pure sucrose is treated with 5 ml of hydrochloric acid (sp gr 1.19), made up to about 100 ml, left at room temperature for several days (e.g., about 1 week at 12° to 15° C or 3 days at 20° to 25° C) and then made up to 1 liter. The acidified 1-percent solution of invert sugar is very stable and retains its titer unchanged for months. A known volume of the standard solution is neutralized with sodium hydroxide and suitably diluted immediately prior to use.

The experimental factor determined by titration, of the standard solution is

$$\frac{\text{Titer}\times\text{mg of sugar per 100 ml}}{100}=F'.$$

F' is then compared with F, the tabulated factor, and the copper solution is adjusted accordingly. If the deviation of the experimental from the tabulated factor is small, it has been the practice of this Bureau to apply the small correction to the tabulated factors rather than to make numerous adjustments of the copper solution.

Carry out the titration as described, find in the table the factor corresponding to the titer and, if necessary, apply to the factor the correction previously determined. Estimate the sugar by

$$\frac{\text{Factor}\times 100}{\text{Titer}}=\text{mg of sugar in 100 ml.}$$

The Lane and Eynon factors are given in tables 85 and 86, pages 590-91.

(2) Applications of the Method.

Determination of reducing sugars in raw sugars containing more than about 0.4 percent of reducing sugars.—A solution of the sample containing 5, 10, or 25 g per 100 ml is titrated against 10 ml of Fehling solution, the percentage of reducing sugar (as invert sugar) being found from table 85. Preliminary treatment with normal lead ace-

tate and potassium oxalate is generally unnecessary except for very low-grade raw sugars.

The sucrose content may be found from the invert-sugar content before and after hydrolysis, which is carried out as described below.

Determination of reducing sugars in refined or raw sugars containing less than about 0.4 percent of reducing sugars.—Twenty-five grams of the sample is dissolved with a quantity of neutralized standard invert-sugar solution containing 0.1 g of invert sugar, and the whole is made up to 100 ml. A convenient procedure is to wash 25 g of the sample into a 100-ml flask containing the requisite quantity of neutralized invert-sugar solution. After solution and completion to volume, the solution is titrated against 10 ml of Fehling solution. The percentage of invert sugar in the sample is found by deducting 0.1 from the percentage of invert sugar in the solution and multiplying the remainder by 4, or it may be found directly from table 87, page 592.

Determination of invert sugar in molasses.—If the sucrose in the sample is to be determined polarimetrically, it is convenient to weigh 65 g of the sample and dilute to 250 ml, using 50 or 100 ml of this solution for determination of reducing sugars, as described below.

Cane molasses.—A solution containing 13 g of the sample is treated with 25 ml of a 10-percent solution of normal lead acetate, made up to 250 ml, shaken and filtered. Fifty milliliters of the filtrate is treated with 5 ml of a 10-percent solution of potassium oxalate, a little alumina cream is added, and the solution is made up to 250 ml, shaken, and filtered. The filtrate, which is free from lead and calcium salts, represents a 1.04-percent solution of the sample and is titrated against 10 ml of Fehling solution. The percentage of invert sugar in the sample is found from table 85 by interpolation between the values given in the columns headed "no sucrose" and "1 g of sucrose per 100 ml."

NOTE.—For purposes of interpolation, a 1.04-percent solution of cane molasses may be taken as containing 0.3 percent of sucrose.

Beet molasses.—One hundred milliliters of a solution of the sample (26 g in 100 ml) is treated with 30 ml of a 10-percent solution of normal lead acetate, shaken, and filtered. The filtrate, representing a solution of the sample of 20 g in 100 ml, is treated with enough solid potassium oxalate (e. g., about 2 g) to remove lead and calcium and filtered. The filtrate is titrated against 10 ml of Fehling solution, the percentage of invert sugar in the sample being found from table 85, column headed "10 g of sucrose per 100 ml." If the sample contains more than 1 to 1.5 percent of invert sugar, the deleaded and decalcified solution should be further diluted with distilled water before titration.

NOTE.—A 20-g sample of beet molasses may be taken as containing 10 g of sucrose.

Determination of sucrose in cane or beet molasses.—Fifty milliliters of the clarified, deleaded, and decalcified 1.04-percent solution of cane molasses obtained as above is treated with 15 ml of 1.0 *N* hydrochloric acid, diluted to about 150 ml, heated to boiling, and kept boiling for 2 minutes. The solution is then cooled, neutralized with sodium hydroxide, and made up to 200 ml. The solution, which now represents a 0.26-percent solution of the sample, may be titrated against 10 ml of Fehling solution, the invert-sugar content being found from table 85,

column headed "no sucrose." The sucrose content of the sample is calculated from the difference between the invert-sugar content before and after hydrolysis. Sucrose in beet molasses may be determined by a similar method.

Determination of reducing sugars in starch, dextrin, and glucose.—For most purposes it is sufficient to assume that the reducing sugars in starch dextrin and starch sugar consist of dextrose. This is determined by titrating a solution of the sample of suitable concentration against 10 or 25 ml of Fehling solution and finding the dextrose content of the solution from table 85 or 86.

If it is desired to determine dextrose and maltose in starch products, the procedure devised by Morris [37] may be used.

Determination of lactose in sweetened condensed milk.—In the analysis of sweetened condensed milk, the determination of lactose by Fehling solution is somewhat affected by the sucrose present. The effect of the sucrose is to reduce the volume of lactose solution required, and it may be allowed for by adding the requisite correction to the burette reading. Tables 85 and 86 give the values for lactose itself, and table 88 shows the burette corrections, in milliliters, for sucrose-lactose ratios of 3:1 and 6:1. At any given part of table 88 the correction is practically proportional to the sucrose-lactose ratio, and the proportionality holds up to a ratio of about 10:1.

(b) SCALES METHOD

(1) General.—Scales [38] devised an iodometric semimicro method of analysis which requires the use of samples of less than 20 mg of monosaccharides or less than 30 mg of diaccharides. The entire analysis is conducted in a single reaction vessel. Scales confined his experimental analyses to dextrose and concluded that each milliliter of iodine represented a constant weight of sugar irrespective of the concentration. He prescribed a 3-minute period of boiling over a free flame or an electric hot plate.

Isbell, Pigman, and Frush [39] employed a modification of the method for determining the reducing powers of a wide variety of sugars. They found that greater precision of analysis was obtained if the period of boiling was increased to 6 minutes. Shaffer and Somogyi (see p. 169) showed that relatively large differences in reaction rates occurred between certain sugars. Hence in order that a uniform method of analysis might be adopted, the time of reaction must be adapted to the most slowly reacting sugar. If the rapidly reacting sugars, dextrose and levulose, are analyzed, it is suitable to shorten the period of boiling to the 3 minutes prescribed by Scales.

Isbell, Pigman, and Frush were unable to verify Scales' statement that each milliliter of iodine represented a constant weight of glucose, irrespective of the concentration of sugar, but found the function

$$f=1.0511+0.0021C+0.000086C^2,$$

in which f is the factor for glucose and C is the titer in milliliters of 0.04 N iodine. The factors for glucose are shown in tables 22 and 23.

The various sugars under strictly comparable conditions reduce different quantities of copper. It may be observed by comparing the reducing values given in table 24 that epimeric sugars give approxi-

TABLE 22.—*Factors for calculating glucose by the Scales method*

Dextrose	0.04 *N* iodine	Sugar factors (average)	Calculated from equation
mg	*ml*		
5	4.69	1.067	1.063
10	9.30	1.075	1.078
15	13.72	1.093	1.096
20	17.92	1.116	1.116
25	21.93	1.140	1.139

mately like reducing values—that is, the configuration of carbon 2 does not materially influence the reducing power. The similarity of epimeric sugars probably arises from the rapidity with which they revert to the common enolic form. Since the groups about carbons 3, 4, and 5 are held more firmly, sugars which differ in the configuration of these carbons are not interconvertible in the alkaline solution and exhibit characteristic properties. Sugars in which the hydroxyl on carbon 3 is *trans* to the hydroxyls on carbons 4 and 5 give the highest reducing powers, while sugars which have *cis* hydroxyls on carbons 3 and 4 give lower reducing values. The differences in the values for lactose, maltose, cellobiose, and turanose show that the configuration of the nonreducing component in the disaccharide molecule influences the reducing power and that the reducing power of the disaccharide may be higher or lower than that of the reducing sugar component. If the glycosidic union is on carbon 3, as in turanose, the molecular reducing power is less than that of the corresponding monosaccharide. If the glycosidic union is on carbon 4, the molecular reducing power is about 1.4 that of the corresponding monosaccharide; and if the glycosidic union is on carbon 6, the molecu-

TABLE 23.—*Factors for various sugars for use with the modified Scales method* [1]

Sugar	Milligrams of anhydrous sugar per milliter of 0.04 *N*-iodine				Sugar	Milligrams of anhydrous sugar per milliter of 0.04 *N*-iodine			
	5-ml titer	10-ml titer	15-ml titer	20-ml titer		5-ml titer	10-ml titer	15-ml titer	20-ml titer
l-Arabinose	1.078	1.092	1.107	1.127	Lactose	1.426	1.434	1.445	1.462
Cellobiose	------	1.383	1.393	1.413	Lactulose	1.460	1.467	1.477	------
d-Fructose	1.040	1.050	1.078	1.097	*d*-Lyxose	------	0.994	1.006	1.024
l-Fucose	------	1.201	1.235	------	Maltose	1.479	1.481	1.485	1.497
d-Galactose	1.215	1.223	1.240	1.267	*d*-α-Mannoheptose	------	1.310	1.328	------
d-α-Galaheptose	------	1.261	1.292	------	*d*-β-Mannoheptose	------	1.312	1.329	------
d-β-Galaheptose	------	1.259	1.283	------	*d*-Mannose	1.075	1.087	1.103	1.126
Gentiobiose	------	1.717	1.731	1.755	Melibiose	1.747	1.757	1.769	------
d-α-Glucoheptose	------	1.291	1.313	------	Neolactose	1.427	1.433	1.440	1.451
d-β-Glucoheptose	------	1.318	1.341	------	*l*-Rhamnose	------	0.973	0.999	------
d-Glucoheptulose	------	1.287	1.322	------	*d*-Ribose	1.049	1.065	1.083	1.106
d-Glucose	1.067	1.075	1.093	1.116	*l*-Sorbose	------	1.171	1.182	------
4-β-Glucosido-mannose	------	------	1.360	1.392	*d*-Talose	------	1.224	1.240	------
d-α-Guloheptose	------	1.291	1.312	------	Turanose	------	2.691	2.714	------
d-β-Guloheptose	------	1.318	1.341	------	*d*-Xylose	0.996	1.007	1.021	1.040
d-Gulose	------	1.152	1.170	------	Invert sugar	1.061	1.067	1.082	1.095

[1] The factors given in this table are the averages of the values obtained in measurements conducted in this laboratory over a period of 8 years. Each value represents not less than 3 determinations. The individual determinations by the same operator did not vary over 1 percent, but the results of different operators varied by as much as 2 percent.

TABLE 24.—*Relative molecular reducing power*[1] (*modified Scales method*)

Sugar	Sample: anhydrous sugar in 10 ml	0.04 *N* iodine solution consumed by Cu_2O	Relative molecular reducing power: glucose=1
	mg	*ml*	
d-Glucose	15	13.7	1.00
d-Mannose	15	13.6	0.99
d-Fructose	15	13.9	1.01
l-Rhamnose	13.7	13.8	1.01
d-Galactose	15	12.2	0.89
d-Talose	15	12.2	.89
l-Fucose	13.7	11.4	.83
d-Gulose	15	12.9	.94
l-Sorbose	15	12.8	.93
l-Arabinose	12.5	11.4	.83
l-Ribose	12.5	11.7	.85
d-Ribose	12.5	11.7	.85
d-Xylose	12.5	12.4	.91
d-Lyxose	12.5	12.6	.92
d-α-Galaheptose	17.5	13.6	.99
d-β-Galaheptose	17.5	13.7	1.00
d-α-Glucoheptose	17.5	13.6	0.99
d-β-Glucoheptose	17.5	13.1	.96
d-Glucoheptulose	17.5	13.3	.97
d-α-Mannoheptose	17.5	13.2	.96
d-β-Mannoheptose	17.5	13.2	.96
d-α-Guloheptose	17.5	13.4	.98
d-β-Guloheptose	17.5	13.1	.96
4-β-Glucosido-mannose	28.5	20.4	1.49
4-β-Glucosido-glucose (cellobiose)	28.5	20.2	1.47
4-α-Glucosido-glucose (maltose)	28.5	19.1	1.39
4-β-Galactosido-glucose (lactose)	28.5	19.5	1.42
4-β-Galactosido-fructose (lactulose)	28.5	19.1	1.39
4-β-Galactosido-altrose (neolactose)	28.5	19.7	1.44
6-β-Glucosido-glucose (gentiobiose)	28.5	16.4	1.20
6-α-Galactosido-glucose (melibiose)	28.5	16.1	1.18
3-α-Glucosido-fructose (turanose)	28.5	10.6	0.77

[1] Ratio of the reducing power of the sugar to the reducing power of glucose.

lar reducing power is about 1.2 that of the corresponding monosaccharide. It may be observed from the results given in table 25 that the molecular reducing powers of the pentoses are slightly lower and of the heptoses slightly higher than the molecular reducing powers of the corresponding hexoses.

TABLE 25.—*Molecular reducing power for configurationally related substances*

Configuration[1]				Average molecular reducing power		
C_2	C_3	C_4	C_5	Pentoses	Hexoses	Heptoses
+	−	+	+	0.91	1.00	1.00
−	−	+	+	.92	.99	.99
+	−	−	+	.83	.89	.96
−	−	−	+	.85	.89	.96
+	+	−	+	--------	.94	.99
−	+	−	+	--------	--------	.96

[1] The configurations of carbons 2, 3, 4, and 5 are indicated by plus and minus signs according to whether the OH lies to the right or left when the formula is written in the conventional manner. For example, the configuration of *d*-glucose is indicated by + − + +. In the case of the pentoses, the sugar has been classified with the configurationally related hexose. Thus *d*-xylose, *d*-lyxose, *l*-arabinose, and *l*-ribose are placed with groups having the (+) configuration for carbon 5.

(2) Method for Making Sugar Determinations.

Reagents.—(1) Dissolve 16 g of copper sulfate ($CuSO_4.5H_2O$) in 125 to 150 ml of water. Dissolve sodium citrate, 150 g of $2Na_3C_6H_5O_7.11H_2O$ or 124 g of $Na_3C_6H_5O_7.2H_2O$; 130 g of anhydrous sodium carbonate; and 10 g of sodium bicarbonate in about 650 ml of water, while warming them slightly to accelerate solution. Cool and combine the two solutions while stirring, make up to 1 liter, and filter.

(2) 0.04 *N* solution of iodine containing 4 percent of potassium iodide.

(3) 0.04 *N* sodium thiosulfate solution containing 0.1 g of sodium carbonate.

(4) Hydrochloric acid solution containing 60 ml of concentrated HCl per liter.

(5) Acetic acid solution containing 24 ml of glacial acetic acid per liter.

Procedure.—To 10 ml of a solution containing 10 to 20 mg of a monosaccharide (or about 30 mg of a disaccharide) and contained in a 300 ml Erlenmeyer flask, add from a fast-draining pipette 20 ml of the copper reagent. Stopper the flask with a two-hole rubber stopper and place over an electric heater or gas flame so regulated that the solution comes to boil in $4 \pm \frac{1}{4}$ minutes. Allow the solution to boil for 6 minutes and then cool it in an ice-water bath for $\frac{3}{4}$ minute while keeping the solution in gentle circular motion. Remove the flask from the ice-water bath, draw up 25 ml of 0.04 *N* iodine solution into a pipette, and while holding the pipette, pour into the flask from a graduate 100 ml of the acetic acid solution, mix gently, and add the iodine solution from the pipette. Then pour 25 ml of the hydrochloric acid solution down the walls of the flask and into the solution. Mix with a gentle circular motion and titrate the excess iodine with 0.04 *N* sodium thiosulfate, using starch as the indicator. Subtract the back titration from the iodine originally added and multiply this value by the sugar factor to give the milligrams of sugar in the sample. For best results each worker should determine his own factors by applying the method to known quantities of sugars. If a large number of determinations is to be made, charts in which the factors are plotted against the titrations may be constructed so that the factor for any titration may be obtained readily.

(c) SCHOORL METHOD FOR INVERT SUGAR IN CANE MOLASSES [40]

Solutions.—Soxhlet solution, p. 170. Deleading solution. Dissolve 7 g of $Na_2HPO_4.12H_2O$ and 3 g of $K_2C_2O_4.H_2O$ and make to 100 ml.

Procedure.—Dissolve 6 g of molasses in water in a 250-ml volumetric flask and defecate with 15 ml of a 10-percent neutral lead acetate solution. Make to volume and filter. Transfer 50 ml of the filtrate to a 100-ml flask and add 5 ml of deleading solution. Make to volume and filter. Pipette 50 ml of the filtrate containing 0.6 g of molasses into a 300-ml Erlenmeyer flask and add accurately 50 ml of Soxhlet reagent. Add one or two fragments of washed and ignited pumice, and place the flask on a wire gauze resting on an asbestos card with a central hole 6.5 cm in diameter. Heat to boiling in 4 minutes and continue the boiling for exactly 2 minutes. Cool rapidly without agitation and add 25 ml of KI solution (20 g in 100 ml) and 35 ml of H_2SO_4 (1 volume of concentrated acid to 5 volumes of water). Titrate

the liberated iodine with 0.1 *N* thiosulfate, using 3 to 4 ml of a 1-percent starch solution as indicator. Determine the blank titration, using 50 ml of water instead of the sugar solution. Deduct the titer of the test sample from that of the blank, and multiply the result by 6.357 to obtain the number of milligrams of copper reduced. Refer the weight of copper to table 96, p. 602, and read the percentage of invert sugar. The table is applicable only to a 0.6-g sample of molasses. A linear interpolation yields accurate results.

(d) METHODS FOR SMALL PERCENTAGES OF INVERT SUGAR IN SUCROSE

(1) OFNER METHOD [41].—(Official method of the Czechoslovakian Republic.)

Reagent.—Dissolve 5.0 g of $CuSO_4.5H_2O$, 10.0 g of anhydrous Na_2CO_3, 300 g of pulverized Rochelle salt, and 50 g of $Na_2HPO_4.12H_2O$ in about 900 ml of water at room temperature, warming slightly at the end of the solution, if necessary. When completely dissolved, it is advisable to heat for 2 hours on the water bath to destroy mold spores. Cool and fill to 1 liter. Treat with active carbon or kieselguhr and filter. Preserve the solution in a dark place.

Sodium thiosulfate.—Dissolve 4.00 g of crystals and make to a volume of 500 ml or, preferably, prepare a stock solution containing in 500 ml, 20.0 g of crystals and 1 ml of *N* NaOH or 0.1 g of Na_2CO_3. Dilute 100 ml to 500 ml, as required. Standardize in the usual way or titrate against the following iodine solution.

Iodine solution.—Dissolve 2.05 g of pure iodine in about 10 g of iodate-free KI dissolved in a few milliliters of water. Make to a volume of 500 ml and preserve in a dark place.

Starch solution.—Rub 2.5 g of soluble starch and about 10 mg of red mercuric iodide in a little water. Dissolve the starch in about 500 ml of boiling water.

Approximately N hydrochloric acid.

Sodium phosphate solution.—Dissolve 100 g of $Na_2HPO_4.12H_2O$ and make to 1 liter. (For lead precipitation.)

Neutral lead acetate.—Dissolve 250 g of $Pb(C_2H_3O_2)_2.3H_2O$ and fill to 1 liter.

Procedure. Refined or affined sugars.—Dissolve 20 g of the sample in distilled water and make up to 100 ml. Transfer 50 ml of the solution to a 300-ml Erlenmeyer flask and add 50 ml of the copper solution. Mix well, add a knife point of pumice or talcum powder, and set on a wire gauze resting on an asbestos card having a central hole 6.5 cm in diameter. Heat to boiling with a Bunsen flame within 4 to 5 minutes and continue the boiling for exactly 5 minutes, diminishing the flame so that only the tip touches the gauze. Cool without agitation by immersion in cold water. Pour from a graduated cylinder 15 ml of 1.0 *N* hydrochloric acid down the wall of the flask, and add immediately a carefully measured volume of the iodine solution (burette or calibrated pipette). The volume of iodine will vary from 5 to 20 ml, according to the amount of copper reduced, but must always be added in excess. After the first few milliliters of iodine have flowed in, the remainder must be added with continuous agitation. Stopper the flask and allow the iodine to react for 2 minutes with occasional agitation. Add 5 ml of the starch solution and titrate the excess of iodine with thiosulfate. Deduct the volume

of the excess iodine from the volume added. One milliliter of iodine solution is equivalent to 1 mg of invert sugar. Ten grams of pure sucrose have, under the conditions of analysis, a reducing power equivalent to 1 ml of iodine; hence deduct 1 ml from the volume of iodine required in the test for reoxidation of the copper. In general, deduct 0.1 ml of iodine for each gram of sucrose in the sample.

Pure sugar sirups.—Prepare a solution containing a known weight of dry substance, preferably 7 to 10 g in 50 ml.

Raw sugar.—Transfer 52 g of the sample to a 200-ml volumetric flask. Dissolve in water, add 2 to 3 ml of neutral lead acetate. Make to volume and filter. Transfer 153.6 ml to a 200-ml flask and add 15 ml of sodium phosphate solution and make to volume. Add 1 g of active carbon, mix thoroughly and allow to stand 15 minutes. Filter and take 50 ml (10 g) of the filtrate for analysis. For the copper analysis take 20 ml of iodine. If the sample contains more than 0.15 percent of invert sugar, take 25 ml (5 g) for analysis. Deduct 0.1 ml from the volume of iodine for each gram of sucrose in the sample.

More impure after-products.—Dissolve 52 g in water, add 4 to 5 ml of lead acetate, fill to 200 ml, and filter. Pipette 153.6 ml into a 200-ml flask, add 20 ml of sodium phosphate solution, make to 200 ml, mix, and filter. Add 1 g of active carbon, mix thoroughly, and allow to stand for 15 minutes. Filter and take for analysis 50 ml or some smaller volume that will contain not more than 15 mg of invert sugar.

Molasses and low-purity sirups.—Dissolve 26 g in water, add 10 ml of neutral lead acetate, fill to 200 ml, mix, and filter. Transfer 153.6 ml of the filtrate to a 200-ml volumetric flask, add 20 ml of sodium phosphate solution, fill to volume, mix, and filter. Add 4 g of active carbon, agitate thoroughly, allow to stand 15 minutes, and filter. Take 50 ml (5 g) of molasses for analysis. Conduct the analysis as described above, but continue the boiling for 7 instead of 5 minutes, since the impurities in low-grade products diminish the rate of reduction of copper. Since 5 g of molasses contains about 2.5 g of sucrose, deduct 0.25 ml from the iodine volume.

Low-grade products frequently contain substances, notably SO_2, which are oxidized by iodine. Ofner, therefore, recommends a "cold" experiment in which the analysis is carried out as described above but with the omission of the boiling period. The iodine consumed in the cold analysis, together with the correction for sucrose, is deducted from the total iodine consumed in the analysis.

(2) Spengler, Tödt, and Scheuer Method [42].

Preparation of stock Müller's solution.—Dissolve 35 g of $CuSO_4.5H_2O$ in 400 ml of boiling water and in a separate container 173 g of Rochelle salt and 68 g of anhydrous Na_2CO_3 in 500 ml of boiling water. Allow both solutions to cool and pour the second solution into the first with agitation. Add 1 to 2 teaspoonfuls of active carbon and after several hours' standing, filter with suction through a hardened filter paper. If copper compounds separate subsequently, the solution must be refiltered.

Procedure.—Transfer 100 ml of a solution containing 10 g of sugar to a 300-ml Erlenmeyer flask, add 10 ml of the stock Müller solution, and heat for 10 minutes in a boiling-water bath. The bath must be heated so strongly that the introduction of the flask does not interrupt the boiling. Adjust the position of the flask so that the level of the

inner liquid surface is at least 2 cm below the outer. Cool rapidly to about room temperature without agitation and add 5 ml of 5 *N* acetic or tartaric acid and then 20 or 40 ml of 0.0333 *N* iodine solution. After the precipitated cuprous oxide is completely dissolved, titrate the excess of iodine with 0.0333 *N* thiosulfate, using a few milliliters of 1- to 2-percent starch solution as indicator.

Conduct a blank analysis with 100 ml of water in the same manner. Deduct the thiosulfate titer of the sugar analysis from the blank titer to determine the volume of 0.0333 *N* iodine used for reoxidation of the precipitated copper. One millititer of 0.0333 *N* iodine equals 1 mg. of invert sugar.

When a series of analyses is conducted, it is obviously necessary to determine the blank only occasionally.

The stability of the thiosulfate solution is increased by the addition of about 3 ml of normal sodium hydroxide per liter of solution.

A deduction of 2 ml of 0.0333 *N* iodine (equals 2 mg of invert sugar) is made to correct for the reducing power of 10 g of pure sucrose and, in general, in the same proportion for smaller weights of sample, for example, for 2.5 g of sucrose a deduction of 0.5 ml is made.

The authors recommend for many cases a "cold analysis," which is conducted in the manner described above except that the heating is omitted. This permits a correction for such impurities as sulfites, which otherwise would be reported as invert sugar.

Ten milliliters of Müller solution contains sufficient copper to oxidize 40 mg of invert sugar, but the authors recommend that samples be taken containing not over 30 mg. Thus if the invert sugar is in excess of 0.3 percent, a correspondingly smaller sample should be taken.

(3) Luff-Schoorl Method [43].—(For determination of invert sugar in cane sugars ranging from 0.3 to 4.0 percent.)

Preparation of copper solution.—Dissolve with gentle heating 17.3 g of $CuSO_4.5H_2O$ and 115 g of citric-acid crystals in about 200 ml of water in a 1–liter volumetric flask. To this solution, after cooling, add with agitation 185.3 g of anhydrous Na_2CO_3 in about 500 ml of water. It is important that the second solution be added to the first and not the first to the second. Make to 1 liter, shake well with 2 g of washed and ignited kieselguhr, and filter with suction. The total alkalinity should be 1.78 *N* (phenolphthalein) and should be controlled.

Procedure.—Transfer to a 300–ml Erlenmeyer flask, 25 ml of the copper reagent and 25 ml of the sugar solution containing 5 g of the sample, or, if necessary, such smaller quantity as contains not more than 45 mg of invert sugar. Add a few fragments of pumice, and place the flask on a wire gauze resting on an asbestos card having a central hole 6.5 cm in diameter. Fit the flask with a reflux air condenser, heat to boiling in 3 minutes, and continue the boiling for exactly 5 minutes. Cool at once without agitation in tap water. To the cooled solution add 15 ml of KI solution (20 g in 100 ml) and 15 ml of H_2SO_4 (25 g of concentrated acid in 100 ml,) in such a manner as to avoid loss by effervescence. Titrate the liberated iodine with 0.1 *N* thiosulfate, using about 1 ml of a 1–percent starch solution as indicator. Make a blank determination, using 25 ml of water in place of the sugar solution. Refer the difference between the volume of 0.1 *N* thiosulfate required by the blank and the sample under test

to table 97, p. 602, to ascertain the corresponding weight of invert sugar in the sample.

Standardization of thiosulfate.—Dissolve 25.5 g of $Na_2S_2O_3.5H_2O$ and 0.2 g of Na_2CO_3 and make to 1 liter. Standardize with pure $K_2Cr_2O_7$.

Weigh accurately about 0.22 g of $K_2Cr_2O_7$ and dissolve in 450 ml of water in a 750-ml Erlenmeyer flask. Add successively 15 ml of KI solution (20 g in 100 ml) and 15 ml of concentrated HCl. Titrate the liberated iodine with thiosulfate, using 3 ml of a 1-percent starch solution as indicator.

$$\text{Normality factor}=\frac{\text{mg } K_2Cr_2O_7}{49.022\times\text{ml thiosulfate}}.$$

5. MICROCHEMICAL METHODS

(a) SOMOGYI MODIFICATION OF SHAFFER AND HARTMANN MICROMETHOD FOR DEXTROSE

Shaffer and Hartmann [44] elaborated in detail a method for the determination of sugar in blood, which was applicable to the analysis of samples containing from 0.07 to 2.2 mg of reducing sugar. The method was subsequently applied to other materials than blood and indeed has been found generally applicable to any material containing reducing sugar. It is particularly serviceable in instances in which it is necessary to conserve the supply of material.

Shaffer and Hartmann copper reagent was prepared by mixing copper sulfate, tartaric acid, and sodium carbonate, the last two substances reacting and releasing carbon dioxide. The solution also contained potassium iodate and potassium iodide in such concentration that it was 0.02 *N* with respect to iodine which was released upon acidification.

Somogyi [8], in a study of the method, found that the amount of copper reduced was in a high degree dependent upon the alkalinity of the solution. Within a narrow range, in which the ratio of Na_2CO_3 to $NaHCO_3$ lay between 7:13 and 2:3 and the pH varied from 9.40 to 9.55, the highest copper values were obtained and the ratio of copper to sugar remained constant. In the Shaffer and Hartmann solution the ratio of carbonate to the bicarbonate formed by the reaction of tartaric acid with sodium carbonate was variable and depended upon the variable amount of carbon dioxide lost. Somogyi therefore modified the Shaffer and Hartmann solution.

Reagents.

Final concentration	Substance	Grams per liter
0.026 *M*	Copper sulfate crystals	6.5
.06 *M*	Rochelle salt	12
.2 *M*	Sodium carbonate (anhydrous)	20
.3 *M*	Sodium bicarbonate	25
.023 *N* I_2	Potassium iodide	10
	Potassium iodate	.80
.1 *M*	Potassium oxalate	18

Dissolve the Rochelle salt, sodium carbonate, and sodium bicarbonate in about 500 ml of water, and into this pour with stirring the copper sulfate dissolved in about 100 ml of water; then add the solution of the other constituents and dilute to 1 liter. (Only the potassium iodate need be weighed accurately.)

Measure 5 ml of the reagent into a large test tube (250 by 25 mm) and add 5 ml of the sugar solution containing not less than 0.1 mg and not more than 2.0 mg of dextrose. Mix by gentle shaking, cover the tube with a small funnel, bottle cap, or glass bulb, and keep it in a boiling-water bath for 15 minutes. Cool by placing in a shallow dish of water until the temperature is lowered to 35° or 40° C. Add with agitation 1 ml of 5 N H_2SO_4 (or its equivalent) and see that all Cu_2O is promptly dissolved. After about 2 minutes, titrate with 0.005 N sodium thiosulfate. A blank titration on 5 ml of the reagent is determined after heating with an equal volume of water.

The difference between the blank and the titration of a determination is equivalent to the copper reduced and thus to the sugar. The corresponding amounts of sugar are given in table 98, p. 603, which is a modified form of the table given in the original article.

Notes.—Details of the determination of sugar in 0.2 ml of blood are given in the reference cited.

A 0.005 N thiosulfate solution cannot be kept unchanged for more than a few days. It is advisable to keep a 0.1 N stock solution and prepare 1:20 dilutions as required.

Any agitation of the test tubes, from the beginning of heating in the water bath up to the addition of acid, should be avoided to minimize reoxidation of cuprous oxide by air.

It is undesirable to cool below 30° C. If the sample contains more than 1 mg of sugar, incomplete oxidation of copper may occur.

In order that the pH of the reagent may remain unaltered, it is important that the sample be neutralized with sodium hydroxide (not carbonate). Phenol red is a suitable indicator and renders the end point of the thiosulfate titration more distinct.

(b) BENEDICT MODIFICATION OF FOLIN AND WU METHOD [46, 47]

Reagents.—Alkaline copper solution.—Dissolve 200 g of sodium citrate and 60 g of sodium carbonate in about 800 ml of water. Then dissolve 6.5 g of pure copper sulfate crystals in about 100 ml of water and add to the former solution with agitation. Add 9 g of ammonium chloride, dilute to 1 liter, and mix.

Tungstic acid color.—Dissolve 100 g of pure sodium tungstate in about 600 ml of water in a liter flask. Add 50 g of pure arsenic pentoxide, then 25 ml of 85-percent phosphoric acid and 20 ml of concentrated hydrochloric acid. Boil 20 minutes. After cooling this, add 60 ml of commercial formalin, 45 ml of concentrated hydrochloric acid, and 40 g of sodium chloride. Dilute to 1 liter and mix.

To 100 ml of the alkaline copper solution add 2.5 to 3.0 g of pure anhydrous sodium sulfite and preserve for use. This solution is not reliable after 1 month.

Procedure.—Transfer 2 ml of the sugar solution and 2 ml of the copper reagent to a Folin and Wu sugar tube. Into another tube transfer 2 ml of a standard dextrose solution containing 0.1 (or 0.2) mg per milliliter and 2 ml of copper reagent. Mix by side-to-side shaking and place the two tubes in boiling water for 5 mintues. Cool by immersion in cold water and add to each 2 ml of tungstic acid color reagent. After 1 to 2 minutes dilute to 25 ml, mix thoroughly, and compare in a colorimeter. The sugar in the unknown solution is calculated by the formula

$$\frac{\text{Depth of column of standard}}{\text{Depth of column of unknown}} \times 10 \text{ (or 20)} = \text{mg per 100 ml.}$$

(c) FERRICYANIDE MICROMETHOD OF HAGEDORN AND JENSEN

Hagedorn and Jensen [48] devised a method particularly for the determination of blood sugar, but which is capable of extension to the analysis of any material containing minute quantities of reducing sugar. The maximum weight of dextrose which can be determined is 0.385 mg.

When ferricyanide in alkaline solution is heated with a reducing sugar it is reduced to ferrocyanide, the amount of reduction being a measure of the amount of sugar taken. The quantity of reduced ferricyanide is determined as the difference between the total and that remaining after the reduction reaction. The determination depends upon the reaction

$$2H_3Fe(CN)_6+2HI=2H_4Fe(CN)_6+I_2,$$

which is reversible but can be made to run quantitatively from left to right by the precipitation of ferrocyanide as a zinc complex:

$$2K_4Fe(CN)_6+3ZnSO_4=K_2Zn_3[Fe(CN)_6]_2+3K_2SO_4.$$

The liberated iodine is then titrated with standard thiosulfate.

The Hagedorn-Jensen method has been used extensively in blood analysis. It is introduced into this circular because of its probable general applicability to other materials than blood. It has the great advantage that ferrocyanide is stable in air and no back oxidation occurs. Miller and Van Slyke [49] point out the disadvantage of the determination of ferrocyanide by difference, and they describe a method of direct titration with ceric sulfate, the end point being determined in the presence of the indicator, Setopaline C (a trade name). However, ceric sulfate gave uncertain results with fructose, which curtails the general applicability of the modification. Shaffer and Williams [50] have described a modification in which the amount of reduction is determined by measuring the potential of the ferri-ferrocyanide electrode. This is extremely rapid and convenient, but is to be recommended only if the number of analyses is great enough to justify the labor of assembling the necessary apparatus. Van Slyke and Hawkins [51], using the Van Slyke-Neil apparatus [52], determined unreduced ferricyanide gasometrically by measuring the pressure of nitrogen evolved by the reaction

$$4K_3Fe(CN)_6+N_2H_4+4NaOH=4K_3NaFe(CN)_6+4H_2O+N_2$$

and have shown that the method can be used rapidly and conveniently for the determination of sugar in both blood and urine. Folin [53] determined the ferrocyanide by a colorimetric measurement of the prussian blue found by addition of ferric chloride to the reaction mixture after completion of the reduction. He also described an effective method for the purification of ferricyanide. Hawkins [54], using the gasometric method, found that the reduction was proportional to concentration for all sugars analyzed except fructose, arabinose, and xylose, in which instances it was proportional up to 0.1-mg concentration. The relative reducing powers are glucose, 1.00; mannose, 1.014; galactose, 0.792; fructose, 0.986; arabinose, 0.949; xylose, 1.019; maltose, 0.725; and lactose, 0.726.

Reagents.—(1) Dissolve 1.65 g of $K_3Fe(CN)_6$, recrystallized and dried at 50° C, and 10.6 g of anhydrous Na_2CO_3. Fill to 1 liter and preserve in the dark.

(2) $ZnSO_4.7H_2O$, 10 g; NaCl, 50 g; and water to 200 ml. Immediately before use, add solid KI in the proportion of 2.5 g per 100 ml to the volume of solution required for the analyses. If added to the stock solution, a separation of iodine occurs with lapse of time.

(3) Acetic acid, 3 ml of glacial acid in 100 ml.

(4) One gram of soluble starch in 100 ml of saturated NaCl solution.

(5) Sodium thiosulfate 0.005 *N*. Dissolve 0.7 g of crystals and make to 500 ml. Standardize frequently by titration against 0.005 *N* KIO_3 (0.3566 g in 2 liters), adding for each 10 ml of iodate solution about 20 mg of KI and a few milliliters of dilute HCl.

Procedure.—Into large test tubes (30 by 90 mm) transfer a sugar solution containing less than 0.38 mg of dextrose, and add water to make a volume of 12 ml. Add accurately 2 ml of the alkaline ferricyanide solution and heat in a boiling-water bath for 15 minutes. Cool and add 3 ml of the potassium-iodide–zinc-sulfate solution and 2 ml of acetic acid. Titrate the liberated iodine, using a microburette and 2 drops of starch indicator.

Conduct a blank determination in the absence of sugar. Refer to table 99, p. 604.

Example.—A sample of sugar required 1.26 ml of thiosulfate, and the blank, 1.86 ml; 2.00 ml of standard iodate required 1.90 ml of thiosulfate. Each titer is multiplied by 2.00/1.90 to reduce it to a 0.005 *N* basis. Corrected titers are, respectively, 1.33 and 1.95 ml. In table 99, 1.33 ml is equivalent to 0.119 mg, and 1.95 ml to 0.008 mg of dextrose. Therefore, the corrected sugar content is 0.111 mg.

6. COLORIMETRIC AND VISUAL METHODS

(a) POT METHOD OF MAIN FOR DETERMINATION OF REDUCING SUGARS IN RAW SUGARS AND SIMILAR PRODUCTS [55]

Main has devised a visual method for the determination of reducing sugars, which is capable of yielding results of high precision and of extending the range of quantitative estimation to very low percentages. The reaction is carried out in large resistant-glass test tubes, 150-mm length by 38-mm internal diameter and weighing 50 to 55 g. In order to avoid back oxidation by air, a series of floats is constructed of similar test tubes having slightly smaller diameter and which make a sliding fit into the others. The barrels of these floats are 100 mm long, and the upper end of each is drawn out to a taper, making a total length of about 170 mm.

The water bath is an ordinary oval iron kitchen pot, tinned inside, the capacity of which is 3 gallons. An overflow is fitted near the upper edge of the boiler, and hot water is added continuously through a "sight feed" to replace loss by evaporation. The temperature of the water must be maintained at the boiling point, for which a large ring gas burner is necessary. While in the water bath, the tubes are supported symmetrically by clips in a carrier.

Two alkaline copper reagents are employed: solution I, for concentrations of invert sugar extending up to 16 percent; solution II, for samples containing a maximum of 0.832 percent.

Solution I.—The usual Soxhlet modification of Fehling solution (p. 170). 10 ml of the mixed reagents are used for the analysis. The results are referred to in table 100, p. 605.

Solution II.—A Soxhlet solution (*A*) as usual, containing 34.639 g of $CuSO_4.5H_2O$ in 500 ml of Soxhlet solution; (*B*) 173 g of Rochelle

salt, 50 g of NaOH, and 14.647 g of $K_4Fe(CN)_6$ in 500 ml of solution. For solution II, mix 1 volume of (*A*), 1 volume of (*B*), and 2 volumes of 5 *N* NaOH. This mixed reagent was designated "L. F. S.", and the results are referred to in table 101.

In the extra-alkaline L.F.S. solution, the ferrocyanide, which is present in the ratio of 1 mole to 4 moles of cupric sulfate, has the function of combining with the reduced copper to form cuprous ferrocyanide and obviates the red coloration that tends to mask the end point as indicated by the methylene blue.

For the standardization of copper solution I, invert sugar is prepared according to the method of Lane and Eynon [36]. Prepare a standard invert-sugar solution by dissolving 9.5 g of pure sucrose, accurately weighed, in about 80 ml of water, adding 5.3 ml of hydrochloric acid (sp gr 1.16, or approximately 10 *N*), and completing the volume to approximately 100 ml. Allow this solution to stand at 22° to 25° C for 3 or 4 days and dilute to 1 liter. From this stock solution, pipette 50 ml into a 250-ml flask, neutralize with sodium hydroxide (approximately 2.5 ml of *N* NaOH), and complete to volume. This solution now contains 0.002 g of invert sugar per milliliter.

Transfer the following solutions to each of three tubes in the order stated: 10 ml of mixed Soxhlet solution (solution I); standard neutralized invert-sugar solution, 24.5, 25.0, and 25.5 ml, respectively; and 2 drops of 1-percent methylene blue.

Mix the contents of each tube by gentle rotation and insert the floats so that they rest on the liquid, care being taken not to entrap any air bubbles. Place the tubes in the carrier and immerse in the briskly boiling water for exactly 5 minutes. Then remove and inspect. In general, one of the three solutions will show complete reduction of copper, while the adjacent one will show a trace of blue. The volume of invert intermediate between these two is taken as equivalent to 10 ml of Soxhlet solution. The precision of standardization and also of analysis can be greatly increased by lessening the intervals between the volumes in the tubes. The mean between the last blue and the first red is always taken as the true result, unless the blue color is actually seen to fade in a tube on removing it from the pot at the end of the 5 minutes. In such case, the actual volume in that tube is taken as the correct figure.

As in other methods, some preliminary idea of the amount of invert sugar present in the sample must be ascertained by using a rough incremental titration or other guide.

For the estimation of small percentages of invert sugar, that is, less than 0.8 percent, L. F. S. solution (solution II) may be used. The table upon which the use of this solution is based overlaps table 100 for solution I, since the latter permits the estimation down to about 0.3 percent. The L. F. S. solution should be standardized against an invert-sugar solution containing 0.025 g per 100 ml; 37 ml of such a solution should decolorize 4 ml of L. F. S. in the presence of 2 drops of methylene blue.

The time of heating for amounts of invert sugar below 0.01 percent must be increased to 10 minutes, as shown in table 101, p. 606.

(b) DE WHALLEY METHOD FOR THE DETERMINATION OF INVERT SUGAR IN REFINED WHITE SUGARS [56]

Range, 0.001 to 0.015 percent, capable of extension to higher percentages by dilution with pure sucrose.

Select test tubes of white glass 6 by ¾ inches having a uniform weight of about 9.4 to 9.6 g. Fit large rubber rings about the tops in order to support them in the water bath. The bath is of sheet copper, 7-inch cube with three holes 1 inch in diameter, the central hole being used for the test and the other two as steam vents. A constant water level is maintained 2 inches below the top of the bath. Heat is applied by a ring burner protected from draught. For accurate work, maintain a constant gas pressure of 3.5 to 3.75 inches of water by means of a pressure regulator.

Prepare accurately solutions of, (1) 0.20-percent methylene blue and (2) 3 *N* sodium hydroxide.

Grind the sample of sugar and transfer 7 g, weighed correctly within 0.05 g, to a clean, dry test tube. Add 6 ml of distilled water, 1 ml. of methylene blue (microburette or calibrated pipette), and 1 ml of the caustic soda solution.

Shake the test tube (closed with a rubber stopper) vigorously for 15 seconds, and immerse in the boiling water bath for exactly 2 minutes. Remove from the bath and compare immediately with the row of standard tubes.

Standards.—Prepare a solution of 19.5 g of $CuSO_4.5H_2O$ in boiled distilled water and make to 500 ml. Measure accurately the following volumes into 50-ml volumetric flasks and add to each 10 ml of ammonium hydroxide (sp gr 0.880; 32.9 percent of ammonium hydroxide by titration) and make to volume.

TABLE 26.—*Standards for use with the de Whalley method*

Invert-sugar standard	Copper sulfate solution	Invert-sugar standard	Copper sulfate solution
Percent	*ml*	*Percent*	*ml*
0.001	40.00	0.007	2.97
.002	24.60	.008	2.26
.003	16.40	.009	1.74
.004	10.66	.010	1.33
.005	7.18	.015	0.50
.006	4.92	-----	-----

7. ELECTROMETRIC METHOD FOR THE DETERMINATION OF REDUCING SUGARS [57, 58]

When a solution of reducing sugar is added to a boiling alkaline copper solution, the potential set up at a platinum electrode during the first part of the titration is represented by the expression

$$E_{Pt}=E_{Cu^{++}\rightarrow Cu^{+}}-\frac{RT}{F}\log_e\frac{[Cu^{+}]}{[Cu^{++}]}.$$

The concentration of cupric ions is governed by the composition of the alkaline tartrate solution and by the removal of copper in the form of insoluble cuprous oxide. The concentration of cuprous ions is determined by the solubility product of cuprous hydroxide. When

all the cupric ions have been removed the potential changes rapidly. This sudden change in potential indicates the end of the reaction between cupric ions and reducing sugar.

A micro application of the electrometric method has been made by Niederl and Müller [59]. They used alkaline copper solutions composed of (A) 3.95 g of $CuSO_4 . 5H_2O$ in 500 ml of solution; (B) 19.75 g of Rochelle salt and 7.4 g of NaOH in 500 ml of solution. For the analysis, they mixed equal volumes of A and B. Their apparatus consisted of two vessels, each containing an alkaline copper solution of the same concentration, in which was immersed a platinum electrode. The vessels were connected by an agar-potassium chloride bridge.

For analysis, 3 to 5 mg of substance is accurately weighed, dissolved in water (1 ml for each mg), and transferred to a microburette. One milliliter of the mixed copper reagent, containing 1 mg of copper is placed in each of the two vessels. A reading is taken on the potentiometer and again after the solution in one vessel is brought to boiling. A preliminary titration is carried out as follows: 0.1 ml of the sugar solution is added, the mixture boiled, and a reading taken again. Additions of the sugar solution are continued until 1.2 ml has been used. In the region of the end point the change of potential is very considerable. The maximum change per 0.01 ml marks the end point. The actual determination is carried out in the same way, but larger volumes of the sugar solution are used until the end point is approached.

Their results are as follows:

Sugar equivalents of 1 mg of copper

	mg
d-Glucose	0.635
d-Mannose	.638
d-Galactose	.770
d-Fructose	.679
Maltose	1.019
Lactose	0.884
Invert sugar	.657

The following method, in which the end point is determined by the change of potential between two thick copper wires serving as electrodes, has been devised by Tryller [60]:

Reagents and apparatus.—(1) Soxhlet solution (I), 34.639 g of $CuSO_4.5H_2O$ made to 500 ml of solution; (II), 173 g of Rochelle salt and 50 g of NaOH made to 500 ml of solution.

(2) Sodium sulfate for cell, 39.415 g of anhydrous Na_2SO_4 made to 1 liter of solution.

(3) An electrode of thick copper wire (about 2 mm in diameter).

(4) A cell of Pyrex-glass tubing (8 mm inside diameter with a plug (8 mm long) of plaster of paris at one end. The plug should be washed with the cell solution in which it should be stored when not in use.

(5) A dead-beat moving-coil galvanometer with central zero.

(6) A press-key.

(7) Burette stand, 250-ml Pyrex flasks, burettes, etc.

Method.—The arrangement consists of a galvanometer wired directly to the electrodes through a press-key. Any convenient

number of flasks may be wired to the same galvanometer. Figure 39 shows the flask and electrode assembly. The 250-ml, flat-bottomed flask is fitted with a cork (7) which holds the thick copper-wire electrode, the tip of the burette (6), the cell (2), and the steam vent (5) in position. A copper wire makes contact between the inner cell and the lead to the galvanometer. The liquid in the inner cell is composed of 5 ml of Soxhlet solution II, 5 ml of sodium sulfate solution, and 40 ml of water. This solution may be made up and stored for short periods of time, the liquid in the cell being changed after every six determinations.

A plaster-of-paris plug lasts for 25 to 30 determinations, after which time its sensitivity is reduced. The changing of the cell is easily carried out by making the hole for the cell a sliding fit and placing the rubber collar (9) around the top and adjusting it so that the plug is immersed to a suitable depth. With this arrangement, the cell may be changed while waiting for the solution to boil. A perforated asbestos slab resting on the shoulder of the flask deflects the hot gases away from the measuring apparatus.

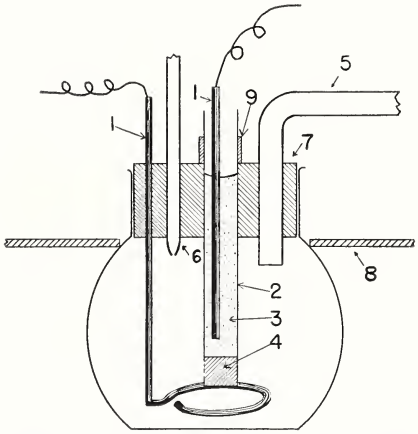

FIGURE 39.—*Assembly for electrometric determination of reducing sugars.*

1, Copper electrode; 2, cell; 3, cell liquid; 4, plaster-of-paris plug; 5, steam vent; 6, burette tip; 7, cork; 8, asbestos; and 9, rubber collar.

In carrying out the determination, the method of Lane and Eynon is followed to the point where methylene blue is added. At this time the press-key is depressed; and, if the galvanometer needle is deflected, the sugar solution is added dropwise. The swing of the needle becomes less and less until finally 1 drop will cause a deflection in the opposite direction. Toward the end of the titration it is advisable to wait 3 to 5 seconds between the addition of 1 drop of sugar solution and the next, as at this point there appears to be a slight lag before the system attains equilibrium.

8. SELECTIVE METHODS

(a) JACKSON AND MATHEWS MODIFICATION OF NYNS METHOD FOR LEVULOSE

Elaborating an observation made by Biourge [61], that at 50° C levulose had, in the presence of Ost reagent, a reducing power 10 times as great as that of dextrose, Nyns [62] determined the copper-levulose equivalents over a wide range of sugar concentrations by heating the reaction mixtures at 48.6° C for 2½ hours. Jackson and Mathews [63] modified the Nyns procedure, shortening the time of reaction by raising the temperature to 55° C and specifying an increased concentration of copper, thus enlarging the range of sugar concentrations which could be analyzed and supplying more rapid methods of copper analysis.

(1) Standard Solutions—

Potassium dichromate.—Prepare a standard solution $N \times 0.1573$, by dissolving 7.7135 g of the pure dry salt and filling to 1 liter. One milliliter is equivalent to 10.00 mg of copper.

Ferrous ammonium sulfate.—Dissolve 61.8 g of the hexahydrate, add 5 ml of concentrated sulfuric acid, and complete to a volume of 1 liter.

Ost solution.—Dissolve 250 g of potassium carbonate (anhydrous) in about 700 ml of hot water and add 100 g of pulverized potassium bicarbonate. Agitate until completely dissolved. Cool and add, with very vigorous agitation, a solution of 25.3 g of pure $CuSO_4.5H_2O$ in 100 to 150 ml of water. Adjust to room temperature, make to 1 liter, and filter.

(2) Analytical Procedure.—Transfer 50 ml of Ost reagent to a 150-ml Erlenmeyer flask. Add by means of an accurately graduated pipette a volume of the solution to be analyzed. This should contain not more than 92 mg of levulose or its equivalent of a levulose-dextrose mixture, remembering that dextrose has about one-twelfth the reducing power of levulose. Add enough water to make the total volume 70 ml. Immerse in a water bath regulated preferably to within 0.1° C at 55° C. Digest for exactly 75 minutes, agitating with a rotary motion at intervals of 10 or 15 minutes.

At the expiration of the prescribed time, filter the precipitated copper on a closely packed Gooch crucible and wash the flask and filter thoroughly without attempting to transfer the precipitate quantitatively. (It is well, however, to transfer all of the loose cuprous oxide, leaving in the flask only the small portion which adheres to the walls.) Remove the asbestos mat by means of a glass rod and transfer to a 400-ml beaker. Add 5 or 10 ml of water and disintegrate the asbestos mat. Add a carefully measured volume of standard potassium dichromate ($N \times 0.1573$) in excess of the volume required to oxidize the cuprous oxide. In many cases the expected amount of precipitated copper will be roughly known, and it will be possible to gage the volume of dichromate which will supply a 3- to 4-ml excess. If the amount of precipitated copper is not even roughly known, it is preferable to add an amount which will supply an assured excess. A very large excess introduces no uncertainty, provided its volume is accurately measured. Of this volume about 1 ml is added to the original reaction flask in order that the residual cuprous oxide may be dissolved and subsequently added to the remainder of the solution. Add to the Erlenmeyer flask by means of a graduated cylinder about 50 ml of hydrochloric acid (1+1). Pour the acidified solution slowly into the 400-ml beaker with constant stirring, and continue to stir until the cuprous oxide is completely dissolved. Wash the Erlenmeyer flask with a jet from the wash bottle, receiving the rinsings in the beaker. Examine the asbestos critically by looking through the bottom of the beaker, which is held above the eye. (If any undissolved cuprous oxide remains, it can be clearly discerned as dark-colored particles.) Immerse the crucible in the acidified solution to dissolve such cuprous oxide as remained in it. Remove the crucible with a glass rod, washing it free of solution. Dilute the solution thus prepared to about 250 ml and electrometrically titrate the excess of dichromate with ferrous sulfate.

The excess of dichromate can also be determined satisfactorily

with the use of the internal indicator, orthophenanthroline, as described on page 184. Indeed, any other method of copper analysis will serve equally well, but in all cases control analyses with pure levulose should be made and a correction applied to bring the copper equivalents into correspondence with table 93, p. 597.

In table 93 is given the correspondence between the reduced copper and the levulose in the sample.

(3) Analysis of Dextrose-Levulose Mixtures.—Jackson and Mathews found that the method, when applied to dextrose-levulose mixtures, lacked perfect selectivity and that it was necessary to apply a correction for the reducing power of dextrose. Throughout the entire range of concentrations 12.4 mg of dextrose proved to have the same reducing power as 1 mg of levulose.

For the analysis of an unknown mixture of dextrose and levulose two equations are necessary for a solution, and Jackson and Mathews recommended a combination of the Lane and Eynon titration for total reducing sugar and the modified Nyns method. The Lane and Eynon titration (25 ml of Soxhlet reagent) is corrected to correspond with the Lane and Eynon table, as described on page 187, and multiplied by the number of milligrams of "apparent" levulose, that is, the levulose equivalent of the copper from table 93. The product, divided by 100, is referred to table 94, p. 599 and the ratio of levulose to total sugar is read from the appropriate column.

(b) HINTON AND MACARA METHOD FOR LEVULOSE IN CONDENSED MILK

Hinton and Macara [64] devised a method which they applied to the determination of levulose in sweetened condensed milk, but which obviously is capable of a more general application. In outline, the method consists in the oxidation of aldose groups to aldonic acids, leaving the levulose unaltered. The levulose is then determined by reducing-sugar analysis. A control solution free of levulose is analyzed simultaneously.

Reagents.—(1) Sucrose solution, approximately 9 g of sucrose per 100 ml (freshly prepared).

(2) Iodine solution, 13 g of iodine and 15 g of KI per 100 ml.

(3) Mixed alkaline solution, equal parts of 2 *N* Na_2CO_3 and 2 *N* NaOH.

(4) Sulfuric acid, approximately 5 *N*.

(5) Sodium sulfite solution, 20 percent by volume.

(6) Dilute sodium sulfite solution, 2 percent freshly prepared; or diluted from 20-percent solution.

(7) Luff solution. Dissolve 25 g of $CuSO_4.5H_2O$ in 100 ml of water; 50 g of citric acid in 50 ml of water; 338 g of $Na_2CO_3.10H_2O$ in 300 to 400 ml of lukewarm water. Add the citric acid solution to the sodium carbonate solution, and then add the copper solution. Mix, cool, make up to 1,000 ml and filter. This solution should be accurately prepared, and 10 ml of the finished solution should require approximately 45 ml of 0.5 *N* sulfuric acid for neutralization to methyl orange.

(8) Iodate-iodide solution, 2.7 g of KIO_3, 30 g of KI and 10 ml of 0.5 *N* NaOH solution per liter.

(9) Potassium oxalate solution.

(10) Sodium thiosulfate solution, 0.05 *N*.

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(11) Soluble starch solution, approximately 2 percent.

(12) Control serum, prepared from fresh milk with the same quantities of ammonia and acetic acid and precipitants as for 40 g of condensed milk, made up to 200 ml and filtered.

Procedure 1, oxidation of aldose sugars.—Pipette 10 ml of the condensed milk serum (zinc serum, page 207) and the same amount of the control serum into 250-ml Erlenmeyer flasks in such a way that the liquid does not flow on the sides of the flasks. To the condensed milk serum add 10 ml of water, and to the control serum add 10 ml of the sucrose solution. Add to each exactly 5 ml of the iodine solution and exactly 6 ml of the 2 *N* mixed alkali solution; mix gently, and allow the flasks to stand for 10 minutes at from 18° to 20° C. Acidify with 1.6 ml of 5 *N* sulfuric acid, and remove the liberated iodine, first, with 20-percent sodium sulfite solution, and finally, after adding 6 drops of starch solution, with the 2-percent sulfite solution. This operation should be conducted as rapidly as possible and with the precision of a titration, although the quantities of sulfite solution need not be measured. When all of the free iodine is eliminated, immediately add 1 drop of methyl orange solution and neutralize with 2 *N* mixed alkali solution. The time elapsing between acidifying with 5 *N* sulfuric acid and neutralizing with the mixed alkali should not exceed 2 minutes to avoid the danger of inversion of the sucrose.

Procedure 2, treatment with Luff solution.—To the contents of each flask add 20 ml of Luff solution; cover with a watch glass and heat the contents to boiling on a plain wire gauze over a burner regulated so that the boiling takes place in 2 minutes; impinging of the flame as hot gases on the sides of the flask should be prevented by an asbestos sheet, with a central hole of suitable dimensions, placed in contact with the wire gauze. When boiling takes place, transfer the flask to an asbestos-covered gauze already heated by a small Bunsen flame, attach a reflux condenser, and maintain gentle ebullition for exactly 10 minutes. Remove from the flame and cool in running water for 4 or 5 minutes.

Titration of reduced copper.—Add exactly 25 ml of the iodate–iodide solution and 20 ml of saturated potassium oxalate solution. Acidify carefully, while swirling, with 20 ml of 5 *N* sulfuric acid. Carefully shake with a rotating motion until the precipitate of cuprous oxide (which is partly converted into white cuprous iodide) has dissolved, and titrate with 0.05 *N* thiosulfate. No further addition of starch should be required. The end point is distinguished by a sharp change to a fine light blue (the color of the cupric salt).

Calculation of levulose.—The difference between the titrations of the sample serum and the control serum, as milliliters of 0.05 *N* thiosulfate solution, multiplied by 0.064, gives the percentage of levulose in the sample, uncorrected for the volume of the clarification precipitate. This factor is strictly correct only for a 20-percent serum, that is, if exactly 40 g of condensed milk is diluted to 200 ml in the preparation of the serum.

(c) SICHERT AND BLEYER MODIFICATION OF BARFOED COPPER ACETATE METHOD FOR MONOSES

Barfoed [65] found that copper acetate in the presence of acetic acid was reduced by monosaccharides but not reduced to any great

extent by the disaccharides, maltose and lactose. Steinhoff [66] modified the Barfoed solution by substituting sodium acetate for the acetic acid. This strongly buffered solution had a pH of 6.4, which remained unchanged during the reduction, whereas the Barfoed solution continually lost acetic acid.

Sichert and Bleyer [67], using Steinhoff solution, formulated a detailed method of analysis which, however, required the use of a specially designed filter. This unnecessary complication has been avoided in the procedure of the Corn Products Refining Co., which, through the courtesy of that company, has been brought to our attention.

Reagents.—(1) Copper solution, 69.28 g of $CuSO_4.5H_2O$ per liter.

(2) Sodium acetate, 500 g of $NaC_2H_3O_2.3H_2O$ per liter.

(3) Ferric sulfate, 120 g of $Fe_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ (or 50 g of $Fe_2(SO_4)_3$) and 100 ml of concentrated H_2SO_4 per liter.

(4) Potassium permanganate, 0.1 *N*, standardized against pure sodium oxalate.

Determination.—Into a wide-necked 250-ml Erlenmeyer flask introduce 10 ml of copper solution, 20 ml of sodium acetate solution, and 20 ml of a sugar solution containing less than 100 mg of dextrose. The flask, equipped with a Bunsen valve, is placed into a calmly boiling water bath for exactly 20 minutes. The flask should be out of line with steam bubbles and should be immersed up to the neck.

Filter the precipitated cuprous oxide through washed asbestos in a Gooch crucible, and wash the flask three times with hot distilled water. It is not necessary to transfer the precipitate quantitatively.

Transfer the crucible to a 150-ml beaker, which bears a mark at 60 ml. Wash the precipitation flask with exactly 20 ml of ferric sulfate solution divided in three portions. Add all washings to the beaker. Care must be taken to dissolve all of the red precipitate. Wash the flask with hot water. Remove and wash the crucible and add water to the 60-ml mark. Bring the solution to boiling on a hot plate, allow to stand 3 minutes, and titrate with permanganate to a pink-gray color, which persists for about 20 seconds. The addition of 1 ml of sirupy phosphoric acid at a late stage of the titration facilitates reading the end point. Refer the volume of permanganate to table 102, p. 607.

(d) MONIER-WILLIAMS MODIFIED BARFOED METHOD FOR MONOSE SUGARS IN CONDENSED MILK [68]

Copper reagent.—Dissolve 60 g of crystallized sodium acetate in water, add 105 ml of *N* acetic acid and make up to 1 liter. Transfer to a dry bottle, add 52 g (or more) of finely powdered crystallized copper acetate, and shake to saturation, and filter.

Ferric sulfate solution.—Dissolve 50 g of ferric sulfate in about 400 ml of water to which 109 ml of concentrated sulfuric acid has been added. Make to 1 liter and filter. Before use, this solution should be treated with 0.1 *N* permanganate until the color of the latter ceases to be discharged.

Clarification.—Transfer to a 100-ml beaker an accurately weighed quantity, approximately 40 g of the well-mixed sample, add 50 ml of hot distilled water (80° to 90° C), mix, and transfer to a 200-ml measuring flask, washing in with successive quantities of water at 60° C until the total volume is 120 to 150 ml. Mix, cool to air tem-

perature, and add 5 ml of dilute ammonia solution (1+9, approx. 1.43 *N*). Again mix, and allow to stand for 15 minutes. Add a sufficient quantity of dilute acetic acid (approx. 1.43 *N*) exactly to neutralize the ammonia added and again mix. Add with gentle mixing 12.5 ml of zinc-acetate solution (21.9 g of $Zn(C_2H_3O_2)_2.2H_2O$+3 ml of glacial acetic acid per 100 ml) and subsequently 12.5 ml of potassium-ferrocyanide solution (10.6 g per 100 ml). Adjust the temperature to 20° C and fill to 200 ml. In all operations avoid the formation of air bubbles. Mix thoroughly, allow to stand for a few minutes, and filter, rejecting the first 25 ml of filtrate.

Determination.—Introduce 25 ml of milk serum (40 g of condensed milk in 200 ml, clarified with zinc ferrocyanide) into a thin-walled boiling tube (8 by 1¼ inches), add 70 ml of the copper solution, mix, cover with a watch glass, and immerse to the level of the liquid in the tube in a large water bath maintained at 80° C for 20 minutes. Remove, cool in running water, filter on asbestos with suction, wash the tube and filter rapidly a few times with freshly boiled water. Dissolve the cuprous oxide in the tube and filter in 20 ml of the ferric sulfate solution. Wash the asbestos pad with cold water and add the washings to the ferric sulfate filtrate. Titrate with 0.1 *N* permanganate to faint permanent pink.

Table 27 is applicable to 25 ml of the milk serum containing 5 g of condensed milk.

TABLE 27.—*Determination of monose sugar in condensed milk*

[5-g sample]

Monose sugar as percentage of condensed milk	Monose sugar in serum	Milliliters of 0.1 *N* permanganate solution for—		
		Levulose	Dextrose	Invert sugar
ml	*mg*	*ml*	*ml*	*ml*
---	0	[a]0.15	[a]0.15	[a]0.15
0.1	5	3.50	2.7	2.8
.2	10	5.50	4.75	4.25
.3	15	7.35	6.0	6.15
.5	25	11.55	8.75	9.85
1.0	50	19.50	15.45	18.0
2.0	100	34.05	25.35	29.45

[a]Blank.

(e) IODOMETRIC DETERMINATION OF ALDOSES

In the presence of iodine in alkaline solution, aldose sugars under suitable conditions are oxidized quantitatively to their respective aldonic acids. The postulated reactions for this oxidation are

$$I_2+2NaOH \rightleftarrows NaIO+NaI+H_2O \tag{49}$$

$$RCHO+NaIO+NaOH \longrightarrow RCOONa+NaI+H_2O. \tag{50}$$

Equations 49 and 50 may be combined to represent the reaction, which is usually written

$$RCHO+I_2+3NaOH \longrightarrow RCOONa+2NaI+2H_2O. \tag{51}$$

It was early recognized that the sodium hypoiodite may also react to form sodium iodate:

$$3NaIO \longrightarrow NaIO_3 + 2NaI. \tag{52}$$

Since sodium iodate cannot oxidize the sugar in alkaline solution, some active iodine is lost from the sugar oxidation reaction, but all the unreduced iodine, that is, all that remains in the form of iodate or iodite, is recovered when the solution is acidified and titrated with standard thiosulfate, thus

$$NaIO + NaI + H_2SO_4 \longrightarrow I_2 + Na_2SO_4 + H_2O$$

$$NaIO_3 + 5NaI + 3H_2SO_4 \longrightarrow 3I_2 + 3Na_2SO_4 + 3H_2O$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6.$$

The difference between the total iodine added and the excess iodine as found by the thiosulfate titration represents the amount of iodine used up in the oxidation of the sugar according to eq 51.

Slator and Acree [69] showed that a check on the iodine value could be obtained by titrating with standard alkali the free acid left after completing the iodine titration.

$$HCl + NaOH \rightarrow NaCl + H_2O.$$
$$\text{Sugar acid lactone} + H_2O \rightleftarrows RCOOH.$$
$$RCOOH + NaOH \rightarrow RCOONa + H_2O.$$

As shown by eq 51, for every two equivalents of iodine used, three equivalents of acid are produced. The final acidimetric titer should then be three halves as great as that of the iodine consumed.

In its earliest form, the method was first devised by Romijn [70], who used buffer salts, such as alkaline carbonates, bicarbonates, phosphates, and borax, to supply the alkalinity in order to avoid the overoxidation which he found occurred with caustic alkali. Later, many investigators who had used buffer salts found that extended periods of time were required to complete the oxidation of the sugar in these weakly alkaline media and that consistent results were not always obtainable. In the most widely used methods, caustic alkali is employed.

The difficulties which must be overcome in standardizing the analytical procedure can be summarized briefly. If the whole required volumes of alkali and iodine are admitted to the sample simultaneously, much of the iodine is transformed to iodate by eq 52. This may leave a deficiency of iodine for the oxidation reaction. If the iodine is present in too great excess, overoxidation can occur. Kline and Acree [71] showed that while the ratio of alkali to iodine consumed by the aldehyde group was 3:2, the ratio in the oxidation of sucrose or levulose proved to be 5:4, indicating that the primary alcohol group was slowly oxidized to a carboxyl group. Conceivably the overoxidation of an aldose proceeds similarly. The rate of addition of the reagents has an important bearing on the results. In the analysis of a mixture of aldose and ketose, such as dextrose and levulose, it is important that the levulose remain unoxidized. If too great an excess of alkali is present the levulose can undergo the Lobry de Bruyn-van Ekenstein rearrangement to dextrose and man-

nose, which are rapidly oxidized by iodine. The time of reaction has undergone endless variation in the specifications, from 24 hours, according to Romijn, to 2 minutes, according to Kline and Acree. Observers agree, however, that in the presence of sodium hydroxide the reaction is rapid, and that short periods of time are sufficient. Space permits the inclusion of only four of the many procedures that have been described.

Method of Willstäter and Schudel [72].—To the aldose solution containing from 1 to 100 mg of sugar, add about twice (1.5 to 4 times) the volume of 0.1 *N* iodine required for oxidation. At room temperature and with effective stirring, add dropwise 1.5 as much 0.1 *N* NaOH as iodine (from alcohol-free sodium hydroxide) and allow the mixture to stand at room temperature for 12 to 15 minutes (for small amounts of sugar, 20 minutes). Add dilute sulfuric acid to slight acidity and titrate the excess of iodine with 0.1 *N* thiosulfate, using starch indicator. Deduct the excess iodine from the volume originally added. The amount of reducing sugar is calculated from the difference where 1 ml of 0.1 *N* I_2=9.00 mg of hexose or 7.50 mg of pentose.

Kline and Acree [71] have criticized the procedure of Willstäter and Schudel on the grounds that the great excess of iodine in general tends to cause overoxidation. Occasional low results are probably caused by the formation of iodate, which removes iodine from the reacting system. Apparently, as Goebel [73] showed, the rate of addition of alkali requires delicate adjustment. If added over a period of 2 to 4 minutes, correct results were obtained. If added more rapidly, the recovery was low.

Method of Kline and Acree [71].—Kline and Acree have devised a procedure by which any considerable excess of either alkali or iodine is avoided, thus eliminating the errors due to iodate formation and overoxidation.

Transfer to an Erlenmeyer flask a weighed sample or aliquot containing approximately 180 mg of aldohexose or 150 mg of aldopentose and neutralize exactly (phenolphthalein, 1 drop only). Add 5 ml of 0.1 *N* iodine from a burette; then add drop by drop from a burette 7.5 ml of 0.1 *N* NaOH. Repeat this process until 22 ml of iodine and 35 ml of alkali solution have been run in, the operation requiring about 5 to 6 minutes. Allow a 2-minute interval for the completion of the oxidation. Acidify with 0.1 *N* (or 0.2 *N*) HCl and titrate the liberated iodine with 0.1 *N* thiosulfate (starch indicator). Add 2 to 3 drops of phenolphthalein and titrate the excess acid with 0.1 *N* NaOH. Deduct the thiosulfate titer from the number of milliliters of iodine added and deduct the hydrochloric acid titer from the number of milliliters of alkali added. The results will be the number of milliliters of iodine and alkali, respectively, consumed by the oxidation reaction. Then 1 ml of iodine equals 9.0 mg of hexose or 7.5 mg of pentose, and 1 ml of alkali equals 6.0 mg of hexose or 5.0 mg of pentose.

Notes.—The ratio of volumes of alkali to iodine should be 3:2 if the reaction is confined to the aldehyde group alone. A departure from this ratio shows that other groups or other substances, such as lignins, are being oxidized. If assurance is had that only sugars are oxidized, and if it is desired to diminish the labor of analysis, either one of the two titrations may be omitted.

The back titration should require about 2 ml of thiosulfate. If the titer exceeds this, it is probable that over oxidation has occurred; if less, an insufficiency of iodine has been added. It is therefore advisable in such instances to repeat the analysis and to use more or less of the reagents, as indicated by the trial analysis.

A small amount of the lactone of the sugar acid is found after acidification, which will result in a fading end point with phenolphthalein. However, when the titration is carried out in a stoppered flask and the alkali is added slowly, a pink color which persists for 1 minute or longer may be taken as the end point.

Lothrop and Holmes method for the determination of dextrose and levulose in honey by the iodine-oxidation method.—Lothrop and Holmes [74] have recommended a procedure which is essentially the same as that of Willstäter and Schudel but specifically adapted to the analysis of honey. They recognized that levulose was slightly oxidized under the conditions of analysis, but the amount of oxidation was found to be an approximately constant percentage (1.2) of the levulose present and permitted the application of an empirical correction. The oxidation of levulose was found to vary rapidly with temperature, and hence the correction applied is valid only for 20° C. Total reducing sugar was determined by the Munson and Walker method and calculated as dextrose. The results agreed with the analysis by the Lane and Eynon volumetric method. In the following detailed procedure, the italicized words have been added to the original text.

To 20 ml of a solution containing 0.2 g of honey add 40 ml of 0.05 N iodine solution, using a 250 ml Erlenmeyer flask. Run in 25 ml of 0.1 N sodium hydroxide *slowly and with continuous agitation*, stopper, and allow to stand 10 minutes at a temperature of 20° C. Acidify with 5 ml of 2 N sulfuric acid and titrate at once with 0.05 N sodium thiosulfate, using starch indicator. The weight of dextrose in grams (not corrected for reduction of iodine by levulose) is found by multiplying the milliliters of 0.05 N iodine reduced by 0.004502. Calculate as follows:

L_A = approximate percentage of levulose,
R = percentage of total reducing sugars calculated as dextrose (Munson and Walker),
D_I = percentage of apparent dextrose (iodometric),
L = true percentage of levulose,
D = true percentage of dextrose.

Then introducing numerical values,

$$L_A = 1.081\ (R - D_I)$$
$$D = D_I - 0.012\ L_A$$
$$L = 1.081\ (R - D),$$

in which the factor 1.081 is the reciprocal of 0.925, the reducing ratio of levulose to dextrose at the nearly constant concentration of reducing sugars specified by the method.

(f) HINTON AND MACARA CHLORAMINE-T METHOD FOR THE DETERMINATION OF ALDOSES [75]

A solution of Chloramine-T behaves like sodium hypochlorite in producing hypoiodite and a certain amount of free iodine when excess potassium iodide is added. It is believed that the reaction takes place

through an intermediate hydrolysis of the Chloramine-T to hypochlorite. The reactions which appear to occur are indicated by the following equations:

$$C_7H_7SO_2Na.NCl+H_2O \rightarrow C_7H_7SO_2H.NH+NaClO$$

$$NaClO+KI \rightarrow NaCl+KIO$$

$$KIO+KI+H_2O \rightarrow 2KOH+I_2$$ (to a small extent before acidification).

The hypoiodite can be used for the oxidation of aldoses.

$$KIO+C_5H_{11}O_5CHO=C_5H_{11}O_5COOK+HI.$$

Upon acidification, the iodine equivalent of the unaltered Chloramine-T, and any unused hypoiodite can be determined by means of thiosulfate.

$$C_7H_7SO_2Na.NCl+2HCl+2KI \rightarrow C_7H_7SO_2H.NH+NaCl+2KCl+I_2.$$

This oxidation proceeds more slowly than when alkaline iodine solution is used and hence it is more easily controlled.

Reagents.—0.05 *N* Chloramine-T solution containing 7.04 g/liter freshly prepared and protected from the light. Standard sodium thiosulfate solution, preferably slightly stronger than 0.05 *N*.

Sodium hydroxide solution, 0.5 *N*.

Sodium hydroxide solution, 0.1 *N*.

Potassium iodide solution, 10 percent.

Soluble starch solution.

Procedure.—Pipette 20 to 25 ml of sugar solution containing about 0.1 g of sugar, into a 250-ml Erlenmeyer flask. Add 20 ml of 10-percent KI solution and 0.8 ml of 0.5 *N* sodium hydroxide followed by 50 ml of 0.05 *N* Chloramine-T solution. Close the flask with a rubber stopper and allow it to stand 1½ hours in a water bath at 17.5° C. Acidify with 10 ml of 2 *N* HCl and titrate at once with standard sodium thiosulfate solution.

1.410 g of iodine=1 g of dextrose.
0.706 g of iodine=1 g of lactose.
.710 g of iodine=1 g of invert sugar.

Sucrose has little effect on the oxidation of aldoses except in mixtures where there is only a small amount of the aldose present. Levulose, although unaffected in neutral solution under the conditions given above, has an apparent iodine equivalent of 0.007. This method has been studied by the authors in its application to condensed milk.

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X. ANALYSIS OF SUGAR MIXTURES

1. INTRODUCTION

For the analysis of a sugar mixture it is generally necessary to have as many different analytical processes as there are sugars. These methods should be selected in such a way that the most varied properties of the sugars are represented. A consideration of some of these properties follows.

Total sugar.—In a relatively few instances, total sugar can be determined in a mixture by densimetric, refractometric, or desiccation methods. Obviously, such methods can be applied only to solutions uncontaminated with nonsugars. The densities and refractive indices of the pure constituents must be known, and in most instances it must be assumed that the properties of the mixture are in linear relation with those of the constituents. In crude materials these methods are more frequently used for the determination of total dry substance than for total sugars and thus are contributory to the determination of purity.

Polarizing power.—This property can be expressed in terms of specific rotation for a monochromatic wave length or as the rotation per gram in 100 ml, in terms of the saccharimetric scale, or as the ratio of the specific rotation of the sugar in question to that of sucrose. For many sugars the specific rotation varies appreciably with concentration, and the tendency at present is to select the concentration of total substance rather than the partial concentration of each sugar in assigning the value of the specific rotation for the calculation. The specific rotations of the sugars are tabulated on page 563.

Reducing power.—For the purposes of calculation, it is convenient to state the reducing powers of the various sugars in terms of that of dextrose. The "reducing ratio" may be defined as the ratio of weights of dextrose to the sugar in question which produce the same weight of reduced copper. Thus by the Allihn method, 240 mg of levulose is required to reduce the same weight of copper as 219.5 mg of dextrose. The reducing ratio of levulose is then 0.915. In the study of starch and its scission products, maltose is frequently used as the unit of

reducing power. In some cases levulose is taken as the sugar of unit reducing power.

Usually the reducing ratios of dextrose to the various sugars vary somewhat with the concentration of sugar. Thus Jackson [1], using the Munson and Walker method, found that the reducing power of levulose varied from 0.912 for 89 mg of copper to 0.937 for 375 mg of copper. With the Allihn method, the ratios appear to be more nearly independent of concentration. Browne [2] found the following reducing ratios for the Allihn method: Levulose 0.915; arabinose, 1.032; xylose, 0.983; galactose, 0.898; invert sugar, 0.958. The ratios for the more common sugars can, for the Munson and Walker method, be calculated from table 78, p. 564. The most comprehensive table of reducing ratios, including both common and unusual sugars, is that of Isbell, Pigman, and Frush (table 23, p. 190), who employed a modification of the Scales method.

2. SELECTIVE METHODS

(a) RECAPITULATION OF PREVIOUSLY DESCRIBED METHODS

Many of the methods of analysis described in detail in previous chapters are selective for the respective sugars and are directly applicable to their determination when they occur in admixture with other sugars. Thus the Clerget method is selective for sucrose and raffinose and is particularly free from analytical error when invertase is used as the inverting agent.

Levulose is selectively determined by the modified Nyns procedure, as described on page 203, but in this case corrections must be applied for the slight reduction by other sugars.

Aldoses can be distinguished from ketoses by oxidation to aldonic acids in mildly alkaline solution (p. 208).

Monoses can with fair approximation be determined in the presence of reducing disaccharides by the modified Barfoed procedure (p. 206).

Pentoses and pentosans upon distillation in the presence of hydrochloric acid yield furfural, which can be estimated as described on page 241.

These selective methods, as well as the general methods described above, can be combined in a great variety of ways for the analysis of sugar mixtures. It is usually true, however, that the application of the selective methods to actual mixtures must be made with caution, since frequently unexpected complications are encountered. It is for this reason that in the following pages will be described only those applications which have been thoroughly studied.

(b) INVERT SUGAR BY POLARIZATION AT TWO TEMPERATURES

By polarization of a solution at two widely separated temperatures, invert sugar or levulose can be determined selectively in the presence of other sugars, since the levulose constituent of invert sugar possesses a high temperature coefficient, whereas the rotatory power of dextrose is independent of temperature. Browne, however, [3, p. 298], points out that 1.5 g of arabinose, 3.0 g of galactose, 7.0 g of maltose, 9.0 g of lactose, or 50 g of sucrose, in 100 ml produces approximately the same change of polarization with change of temperature as 1 g of levulose or 2 g of invert sugar. In some instances, the

partial change of rotation of these sugars with temperature can be applied as a correction.

Gubbe's [4] comprehensive formulas for the specific rotation of invert sugar can be solved for the change of its rotation with change of temperature or for the temperature of complete inactivation. This inactivation is due to the fact that since the rotatory power of levulose diminishes with increasing temperature, while that of dextrose remains constant, there is some temperature at which the two rotations are equal and opposite. Gubbe's formulas

$$[\alpha]_D^{20} = -19.657 - 0.0361C \tag{53}$$

$$[\alpha]_D^{t} = [\alpha]_D^{20} + 0.3246(t-20) - 0.00021(t-20)^2 \tag{54}$$

indicate that the specific rotation at 20° C is variable with concentration but that the temperature coefficient is independent of concentration. The temperature of inactivation therefore is not a constant but a function of concentration.

Browne [3] has calculated that the temperature of inactivation varies with concentration of invert sugar from 83.2° C for 2 g to 90.2° C for 60 g in 100 ml. For general purposes, 87° C is usually taken as the temperature of optical inactivity of invert sugar.

On the other hand, the temperature coefficient of the rotation of invert sugar is 0.0180° S for each gram in 100 ml, regardless of concentration. Hence invert sugar without any assumption of a temperature of inactivation can be determined by

$$\frac{P'-P}{0.0180(t'-t)} = \text{grams in 100 ml,} \tag{55}$$

in which P' is the saccharimetric reading at t' and P the reading at t in a 200-mm column. Obviously, any pair of temperatures sufficiently separated will serve for the determination.

The suggestion seems valid that the method of determination by temperature coefficient is more reliable than that of polarization at the temperature of inactivation. Not only is there considerable experimental difficulty in accurately maintaining a temperature of 87° C, but there remains the uncertainty that inactivity has been attained. The method of temperature coefficient is free from these uncertainties, since any pair of temperatures will serve, provided they are accurately observed.

After the temperature coefficient has been determined, the invert sugar is calculated by formula 55. If it is desired to determine the other constituent of the mixture, the rotation of the invert sugar at 20° C (P_{20}) can be substituted into the low-temperature polarization by reference to table 76, p. 563, which is computed from the Gubbe specific rotation formula 53, in which C refers to the concentration of total solids in 100 ml. The third column gives the rotation which each gram of invert sugar contributes to the total rotation at various concentrations of sugar. Note that these values are expressed in saccharimeter degrees. P_{20} so found can be transformed to P_t, if necessary, by formula 55. The rotation of invert sugar is deducted algebraically from the observed polarization, leaving a remainder which represents the rotation of the second constituent. If there is an excess of dextrose, it can be calculated quantitatively

by dividing its rotation by that of 1 g of dextrose at the concentration of total sugars in the mixture. The rotation of dextrose can be selected from table 74, p. 562.

Frequently the second constituent of the mixture is commercial glucose. This product as manufactured in this country is a liquid of density varying from 41° to 45° Baumé, and has a specific rotation varying from 100° to 125°. Obviously no exact determination is possible by means of polariscopic measurement, but if a specific rotation of say 108° is arbitrarily assumed, a measure of the constituent is obtained by dividing the observed rotation (corrected by deducting the rotation of the invert sugar) by 0.1600, the polarization of 1 g of the liquid product. The analyst should always state the specific rotation which is assumed for the purpose of calculation.

Any other probable specific rotation can be assumed for the purposes of this calculation, and the appropriate divisor can be found in table 28, which is taken from Browne's Handbook of Sugar Analysis [3].

TABLE 28.—*Rotatory power of commercial glucose*

$[\alpha]_D$ (for liquid product)	Polarization of 26 g in 100 ml	Liquid in 100 ml giving a rotation of 1° S	$[\alpha]_D$ (for liquid product)	Polarization of 26 g in 100 ml	Liquid in 100 ml giving a rotation of 1° S
Degrees	° *S*	*g*	*Degrees*	° *S*	*g*
+125	188.0	0.1383	108	162.5	0.1600
120	180.5	.1440	105	157.9	.1647
115	172.9	.1503	100	150.4	.1729
110	165.4	.1572			

(c) LEVULOSE BY POLARIZATION AT TWO TEMPERATURES

By the procedure outlined in the previous section, levulose can be determined by polarization at two temperatures. The change of rotation of 1 g of levulose per degree change of temperature should be exactly twice as great as that of invert sugar, or 0.036. Wiley [5] gives the value 0.0357. The average computed value of five previous investigations [3] is 0.0362, the difference between the extreme values being about 20 percent. On the other hand, Jackson and Mathews [6] in an extended investigation found experimentally between 20° and about 70° C a coefficient of 0.03441. The value was found to be independent of concentration between 3 and 18 g of levulose in 100 ml. There is thus an outstanding discrepancy of 4.5 percent between the older values of the temperature coefficient and the recent experimental determination of Jackson and Mathews. The lower value of the coefficient has been closely verified by Lothrop [7], who found in a limited number of experiments between 20° and 70° C a mean value of 0.0341. By application of the Jackson and Mathews coefficient, 0.03441, to the analysis of levulose in honey, Lothrop found a close agreement with the levulose percentage as determined by chemical methods.

This important coefficient requires further investigation. Not only is it divergent from Wiley's value, but it is inconsistent with the invert-sugar coefficient, 0.018, which should be exactly half that of levulose. It is apparent that the coefficient remains constant with varying concentration of sugar, but to what extent it is constant between different temperature intervals is at present undetermined.

Until further investigations are made, it is to be recommended that the temperature interval 20° to 70° C be employed with the coefficient 0.03441, that is, 1 g of levulose in 100 ml of solution in a 200-mm column diminishes 0.03441° S for each degree rise of temperature. The mean expansion coefficient between these temperature limits is, according to Jackson and Mathews, 0.00044. Thus if the higher temperature is exactly 70°, the observed polarization must be multiplied by 1.022 before subtracting from the polarization at 20° C. The decrease in the corrected polarization divided by 0.03441 yields the number of grams of levulose in 100 ml of solution.

(d) GALACTOSE BY MUCIC ACID PRECIPITATION

Galactose is oxidized by nitric acid to yield about 75 percent of mucic acid. Under closely specified conditions of analysis, the quantity of recovered mucic acid is reproducible and can be related empirically to the quantity of galactose in the sample. The method is applicable to free galactose or to the combined galactose in compound sugars or in galactans. Certain glycosides containing galactose, for example, saponins, yield insoluble products upon hydrolysis. Such glycosides must first be hydrolyzed with sulfuric acid (2 to 5 percent) and the insoluble material separated by filtration [8].

van der Haar [8] has given detailed specifications for the analytical procedure. Transfer the weighed sample containing galactose to a beaker (12 cm in height and about 60 mm in diameter) and add sufficient sucrose to increase the weight of total sugar to 1.000 g. Add 60 ml of nitric acid (sp gr 1.15 at 15° C) and place the beaker in an inclined position in a boiling-water bath and with repeated agitation allow it to remain until the weight of the contents has diminished to somewhat less than 20 g (that is, 19.8 to 20). Cool, and add water to make the weight exactly 20 g. Add 500 mg of pure, dry mucic acid and allow to stand for 48 hours at approximately 15° C, during which time stir occasionally. During the last few hours, adjust the temperature to exactly 15° C. Filter the precipitated mucic acid with suction on a weighed Gooch crucible prepared with asbestos which has previously been treated with nitric acid. Wash the precipitate four times with 5 ml of a solution of mucic acid saturated at 15° C and finally with 5 ml of water. Dry the precipitate at 100° C to constant weight. Deduct 500 mg from the weight of the precipitate and refer the result to column 3 of table 103, p. 608.

Acree [9] states that the oxidation of galactose by nitric acid is accelerated by the oxides of nitrogen, hence if the nitric acid is too pure it is preferable to add a small quantity of nitrous acid or an alkali nitrite.

(e) DETERMINATION OF MANNOSE AS PHENYLHYDRAZONE

While all reducing sugars are capable of forming hydrazones, the hydrazone of mannose is particularly insoluble and thus is suitable for its quantitative estimation. Bourquelot and Hérissey [10] prescribe the conditions of analysis. About 1 g of mannose dissolved in 16.6 ml of water is treated with a solution of 1.2 ml of phenylhydrazin and 1.2 ml of glacial acetic acid made up to 6 ml with water, and allowed to stand for 8 hours at a temperature not above 10° C. The hydrazone is collected on a Gooch crucible and washed with 15 ml

of ice water, 10 ml of absolute alcohol, and 10 ml of ether. The precipitate is dried in a vacuum over sulfuric acid. One gram of mannose yields theoretically 1.5 g of phenylhydrazone.

The hydrazone is soluble to the extent of 40 mg in 100 ml of solution and a small correction for this solubility increases the precision of analysis.

Pellet [11] has found the method suitable for the estimation of small amounts of mannose in cane molasses.

(f) DETERMINATION OF ARABINOSE AS DIPHENYLHYDRAZONE

Neuberg and Wohlgemuth [12] have made use of the high insolubility of arabinose diphenylhydrazone for estimating arabinose in the presence of other monosaccharides. Mannose or fucose in excessive quantities are apparently the only sugars which interfere with the selectivity of the analysis. The authors illustrate the method by the following example.

A solution (100 ml) containing dextrose, fructose, xylose, glucuronic acid, and 1.0066 g of arabinose was evaporated to 30 ml. The resulting solution was heated on a water bath for ½ hour with 6 g of diphenylhydrazine in 50 ml of 96-percent alcohol with additions of very dilute alcohol or preferably with a reflux condenser. The solution was cooled and allowed to stand for 24 hours. The precipitated hydrazone was collected on a Gooch crucible, washed with 50 ml of 50-percent alcohol, dried, and weighed. Yield, 2.1143 g of hydrazone, equivalent to 1.0035 g of arabinose. Factor, 0. 4747.

(g) DETERMINATION OF URONIC ACIDS

The uronic acids, glucuronic and galacturonic, are widely distributed in both plants and animals. They play an important role in the carbohydrate metabolism of the cell wall. Dickson, Otterson, and Link [13] have found that free glucuronic acid is present within the cell of corn seedlings and that a polymerized glucuronic acid sometimes associated with the cellulose, comprises part of the pectinaceous substance of the cell and cell wall. Nanji, Patin, and Ling [14] found that purified pectin preparations contained from 70 to 73 percent of uronic acid anhydride. Browne and Phillips [15] showed that uronic acids comprised about 3 percent of sugar-cane bagasse and that sugar-cane juice contained from 0.1 to 0.6 percent (based on ash-free solids) of uronic acids, the variations depending upon the methods of maceration. In cane molasses the uronic acids were found concentrated to an average of about 2 percent. These authors believed that the uronic acids are derived from pectins which are extracted with the juice.

When a uronic acid is heated with hydrochloric acid, decarboxylation occurs with the formation of furfural and carbon dioxide according to the equation

$$C_6H_{10}O_7 = C_5H_4O_2 + CO_2 + 3H_2O.$$

The yield of furfural is less than the theoretical, while that of carbon dioxide is quantitative. In the absence of other reactions yielding carbon dioxide, a measure of the gas evolved serves for the quantitative determination of uronic acid.

Whistler, Martin, and Harris [16] in a study of the determination of uronic acids in cellulosic materials, found that under the drastic conditions employed in the analysis, carbohydrates free from uronic acids were slowly but regularly decomposed with the formation of carbon dioxide, necessitating the application of a correction.

The method of determination was originally devised by Lefèvre and Tollens [17]. Dickson, Otterson, and Link [13] further elaborated the method, measuring the carbon dioxide by absorption in barium hydroxide and titration of unreacted alkali.

The details of the method described here are those of Whistler, Martin, and Harris [16], who adapted the procedure specifically to the determination of uronic-acid groups in cellulosic materials. Their procedure can, however, be used without modification for any other material by selecting a weight of sample which will yield 30 to 40 mg of carbon dioxide.

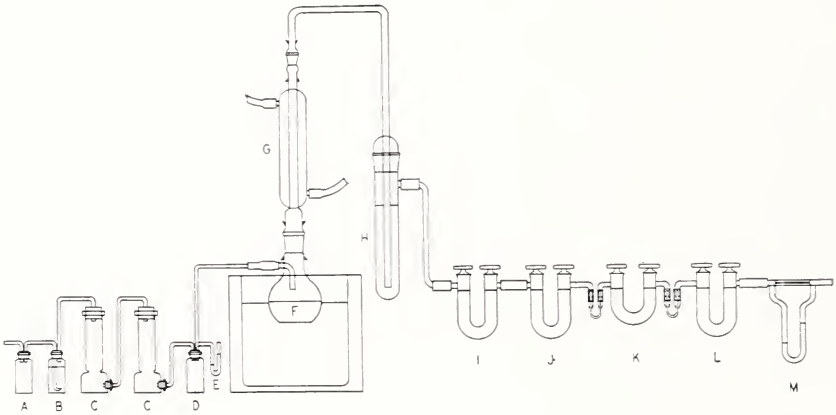

FIGURE 39 (a).—*Apparatus for determination of the rate of evolution of carbon dioxide from uronic acids or materials containing uronic acids during treatment with hydrochloric acid.*

The apparatus is not drawn to scale. See original article for dimensions.

The apparatus is shown in figure 39 (a). Nitrogen, which is used as the carrier gas for the evolved carbon dioxide, enters the apparatus through an empty safety bottle, *A*. It next passes through an alkaline solution of pyrogallol, *B*. The inlet tube in this bottle is drawn out to a small orifice, which produces very fine bubbles. From *B* the gas passes through two absorption towers, *C*, filled with soda lime, into a second safety bottle, *D*, which is provided with a mercury manometer, *E*, and then enters the reaction flask, *F*, by way of a side arm whose outlet is 10 to 15 mm above the surface of the liquid in the flask. The size of the flask depends upon the type of material and the size of the sample to be analyzed. In most experiments a 500-ml reaction flask is suitable. From the reaction flask the gas passes through a 40-cm reflux condenser, *G*, and into a bubbling tower, *H*, containing approximately 60 ml of concentrated sulfuric acid. The sulfuric acid serves to remove interfering decomposition products which are carried over from the reaction flask. The gas next passes through the U-tube, *I*, which is filled with anhydrous copper sulfate to remove chlorine or hydrogen sulfide, then through the tube, *J*,

which contains phosphorus pentoxide, and finally through the carbon dioxide–absorption tube, *K*, containing Ascarite, backed by phosphorus pentoxide. The absorption tubes, *K*, are connected into the train by means of mercury-cup seals [18]. This type of connection makes possible a rapid exchange of the absorption tubes. Tube *K* is protected by a soda-lime tube, *L*, which is followed by a calibrated flowmeter, *M*, for estimating the rate of flow of nitrogen through the apparatus.

The reaction flask is immersed in a vessel containing about 16 liters of hydrogenated cottonseed oil. A bath temperature of 130° C was found to be optimum for maintaining a steady but gentle boiling of the reaction mixture. The bath is brought to the operating temperature by means of two electric immersion heaters, one of 500 and one of 1,000 watts. When the desired temperature is reached, the 500-watt heater alone is sufficient to maintain thermal constancy within ±0.2° C. The time required to raise the temperature of the bath to 130° C is approximately 50 minutes.

The flask is placed in position in the oil bath so that the oil level is 3 to 4 mm lower than the liquid level inside the flask. This precaution is taken to prevent the baking of small bits of sample which may be splashed against the sides of the flask. Nitrogen, at the rate of about 10 liters per hour, is passed through the apparatus until the Ascarite tube, *K*, shows no further gain in weight. This operation requires about 30 minutes, during which time the temperature of the oil bath is slowly raised to 50° C. When the apparatus is free of carbon dioxide, both heating units are turned on and the temperature is brought to 130° C. This procedure is always carefully followed in order to assure the same preliminary heating for all samples. The point of zero time is taken as the time at which the bath reaches 130° C. At that time the Ascarite tube, *K*, is removed for weighing and a second weighed Ascarite tube inserted in its place. At the end of 1 hour the second tube is removed for weighing and replaced by the first. This process is repeated at intervals of 1 hour for the duration of the analysis. When analyses are made of pure uronic acids or materials rich in uronic acids, a small amount of carbon dioxide is evolved by the time the temperature of the bath reaches 130° C. In these cases, this amount is measured and added to that evolved during the first hour.

Since the rate of evolution of carbon dioxide is appreciably affected by variations in acid strength, it is essential that the same concentration (within 0.02 percent) of hydrochloric acid be used in all analyses. The acid should be accurately 12 percent, or 3.290 *N*.

To determine the correction for the carbon dioxide evolved by decomposition of carbohydrates other than uronic acids, weigh the Ascarite containers hourly until the rate of increase in weight is constant. The constant rate of evolution indicates that the carbon dioxide is being derived solely from the uronic acid-free carbohydrates. Calculate from the determined increase per hour the total weight of carbon dioxide which was evolved during the period (3 to 5 hours) before the rate became constant, and deduct the computed weight from the total evolved during this period. The weight of carbon dioxide times 4.00 equals the weight of uronic acid anhydride.

323414°—42——16

3. DETERMINATION OF TWO SUGARS IN A MIXTURE

(a) TWO SUGARS BY COMBINATION OF TWO POLARIMETRIC EQUATIONS

In many instances it is possible to polarize a sugar mixture under conditions sufficiently different to emphasize some striking difference in the properties of the two sugars. The variation in specific rotation of the two individuals under the varied conditions must be known in order to substitute in the two corresponding equations. If x and y are the respective percentages of each sugar in the mixture, a and a' the known specific rotations of one of the sugars under the two varied conditions, and b and b' those of the second sugar,

$$ax+by=100[\alpha]_D \tag{56a}$$
$$a'x+b'y=100[\alpha]_D', \tag{56b}$$

in which $[\alpha]_D$ and $[\alpha]_D'$ are determined experimentally. The specific rotations can obviously be replaced by the saccharimetric constants.

While it is possible theoretically to determine both constituents of a mixture by the procedure outlined, the method is most frequently used to determine one constituent selectively in the presence of an optically active impurity. Thus the Clerget method, which has been described in detail, is employed for the determination of sucrose in the presence of invert sugar. Theoretically, it should be possible to calculate the invert sugar also, but it is at present difficult to assign with confidence a definite value to the specific rotation of invert sugar, since our knowledge of the partial rotatory powers of the constituents of sugar mixtures is incomplete.

The principle of the method is used in the determination of mixtures of sucrose and raffinose by the Creydt raffinose formula, which would yield exact results for both constituents but for the complication that usually a third group of optically active substances, namely aminoacids, contaminates the product which is subjected to analysis.

Other examples of the use of two polarimetric equations have been cited in the description of the determination of levulose and invert sugar by polarization at two temperatures. In some instances the second constituent of the mixture can be determined by calculation from the residual rotation obtained by deduction of the rotation of the determined constituent from the observed rotation.

(b) TWO SUGARS BY COMBINED POLARISCOPIC AND REDUCTION EQUATIONS

(1) Browne Formulas.— A thorough study of the determination of two sugars in a mixture by a combination of polariscopic and reducing-power methods has been made by Browne [2] and [3, page 475]. Reducing sugars are determined by the Allihn method and polarizations, observed in a 200-mm column, are stated in terms of Ventzke sugar degrees. Browne showed that by the Allihn method the reducing power of a sugar mixture is a strictly additive property of the constituents. The assumption is made tacitly that the polarizing power is also additive.

If the reducing ratio of sugar A to dextrose is a and of sugar B is b, then in a mixture of x percent of A and y percent of B, the combined influence is

$$ax+by=R,$$

in which R is the percentage of total reducing sugars determined as dextrose.

If the relative polarizing power of sugar A is α and that of B is β, then, in the mixture, $\alpha x+\beta y=P$, in which P is the polarizing power of the mixture of sugars expressed in Ventzke degrees. Hence

$$x=\frac{\beta R-bP}{a\beta-\alpha b}$$

$$y=\frac{aP-\alpha R}{a\beta-\alpha b}=\frac{R-ax}{b}.$$

Relative polarizing power (α and β) is defined as the ratio of specific rotation of the sugar in question to that of sucrose. The values of α and β for 20° C and a concentration of 10 percent are given in table 29. For levulose and galactose these values vary considerably with concentration and temperature and must be calculated by the formulas

$$\text{Levulose } \alpha=-1.3393-0.00166p+0.0085(t-20),$$
$$\text{Galactose } \beta=1.210+0.0012(p-10)-0.00315(t-20),$$

in which p is the percentage of the sugar in the solution polarized.

TABLE 29.—*Constants applicable to the Browne method of analysis of sugar mixtures*

Mixture	a	b	α	β	Denominator ($a\beta-\alpha b$) at 20° C and 10 percent
Levulose (A), glucose (B)	0.915	1.00	−1.356	0.793	+2.082
Glucose (A), galactose (B)	1.00	0.898	0.793	1.21	+0.498
Levulose (A), galactose (B)	0.915	.898	−1.356	1.21	+2.325
Levulose (A), arabinose (B)	.915	1.032	−1.356	1.571	+2.837
Xylose (A), arabinose (B)	.983	1.032	0.283	1.571	+1.252

The constants required for calculation are given in table 29. The list is capable of extension as the constants for other sugars are determined. The values tabulated under a and α refer to the sugar A and those under b and β to the sugar B.

Example.—A solution containing 4.52 percent of levulose and 4.84 percent of dextrose rotated −2.15° V in a 200-mm tube at 22° C and showed a reducing power equivalent to 9.06 g of dextrose. By the above formula, $\alpha=-1.3378$. Then

$$x \text{ (percentage of levulose)}=\frac{0.793\times 9.06-(-2.15)}{0.915\times 0.793-(-1.3378)}=4.524.$$

$$\text{(percentage of dextrose)}=9.06-(0.915\times 4.524)=4.92.$$

(2) MATHEWS FORMULA.—The most commonly occurring mixture of two sugars which can be analyzed by a combination of reducing and polarizing equations is that of dextrose and levulose. Mathews [6, p. 433] has derived a formula which permits a ready calculation of the ratio of levulose to total reducing sugar when the sample has been polarized in a saccharimeter and its reducing power determined by the Lane and Eynon method of titration. The method of calculation is valid under the assumptions that no optically active or reducing substance other than dextrose and levulose is present in the sample, and that the rotation of the mixture is the algebraic sum of the rotations of the constituents whose specific rotations are referred to the concentration of total sugar rather than to the partial concentration of each.

While the method of determination strictly applies only to pure mixtures of dextrose and levulose, it may frequently be applied to crude mixtures, such as fruit juices, to yield a proximate analysis. At this Bureau the method has been applied to numerous samples of hydrolyzed juices of the jerusalem artichoke for rapid proximate analysis. The sugar mixture in such products consists of about 70 to 80 percent of levulose, about 20 to 25 percent of dextrose, and a small quantity of dextrorotary difructose anhydrides, which introduces an error of about 2 percent into the analysis. Application of an empirical correction diminished the error considerably.

The procedure is simple. If the levulose content is high, prepare a sample containing 15 to 20 percent of sugars, or somewhat more if dextrose is the predominating sugar. Polarize in a 200-mm tube, preferably at 20° C. Dilute a measured aliquot to such volume that the resulting solution contains about 0.5 g of sugar per 100 ml and titrate against 25 ml of mixed standardized Soxhlet solution by the method of Lane and Eynon. If necessary, correct the burette reading to conform to an exactly standardized Soxhlet reagent. The method of calculation is greatly facilitated by use of table 95, p. 601.

Example.—Assume that a solution of levulose and dextrose polarized −43.8°S at 20° C, and that 5 ml of this solution diluted to 100 ml gave a Lane and Eynon titration (25 ml of Soxhlet solution) of 26.18. Then $D=100/5=20$ and $\frac{PT}{D}=\frac{-43.8\times 26.18}{20}=-57.3$.

By table 95, p. 601, the approximate ratio is 89.8 percent, and the correction factor, f, is −0.80. The correction is

$$\frac{f\times D}{T}=\frac{-0.80\times 20}{26.18}=-0.6,$$

and the true ratio is $89.8-0.6=89.2$. The concentration of total sugar is calculated in the usual way from the titer

$$\frac{100F}{T}=\frac{100\times 127.0}{26.18}=485.1 \text{ mg per 100 ml}$$

of the solution titrated. The concentration of total sugar in the polarized solution is

$$0.4851\times 20=9.702 \text{ g per 100 ml.}$$

Levulose is

$$9.702\times 89.2 \text{ percent}=8.654 \text{ g per 100 ml,}$$

and dextrose is

$$9.702\times 10.8 \text{ percent}=1.048 \text{ g per 100 ml.}$$

(c) TWO SUGARS BY COMBINATION OF TWO REDUCTION EQUATIONS

(1) General.—For analysis of two sugars in a mixture, advantage is frequently taken of differences in reducing action which the individual sugars show under different conditions of analysis. In many instances the difference in behavior between the two sugars is so marked that one sugar can be determined selectively. In most cases the accompanying sugar produces minor effects, and corrections are required for accurate analysis. Thus Jackson and Mathews in their modification of the Nyns method found that 12.4 mg of dextrose reduced as much copper as 1 mg of levulose, but that this constant correction could be applied with certainty.

The variety of combinations by which this analysis can be conducted is considerable, but quite invariably one process is the de-

termination of total reducing sugar. The remaining methods of analysis can be chosen from the group of selective methods, but should take advantage of some property which the accompanying sugar lacks.

(2) Sucrose and Lactose in Dairy Products by Two Reduction Processes.—An interesting method for the simultaneous determination of sucrose and lactose in sweetened condensed milk and ice cream has been described by White [19]. In outline, the clarified solution is subjected to the Munson and Walker method of lactose analysis and the copper referred to the appropriate column of lactose-sucrose mixtures. The filtrate from the cuprous oxide, which is then free from lactose, is collected quantitatively, acidified, and heated to invert the sucrose, which is then determined in the form of invert sugar by a second reducing-sugar analysis. Inasmuch as a portion of the sucrose is destroyed during the lactose analysis, an empirical correction is applied to the cuprous oxide precipitated by invert sugar. The method is given in the following brief example:

Weigh 10 g of condensed milk (20 g of ice cream) into a 250-ml volumetric flask and dissolve in 125 ml of boiling water. Mix for 3 minutes, cool to 20° C and add gradually 10 ml of Soxhlet copper-sulfate solution and 6 ml of 0.5 *N* sodium hydroxide. Make to 1.5 ml over the mark (3.2 ml for ice cream) and filter.

Determine lactose in 50 ml of the filtrate by the Munson and Walker method, using the "1 lactose—4 sucrose" column. Collect the filtrate from the cuprous oxide precipitate in a 250-ml flask and wash with 80 ml of hot water. Add 34 ml of 1+1 hydrochloric acid and invert in a boiling water bath for 5 minutes. Cool and neutralize with 50-percent sodium hydroxide. Determine invert sugar by Munson and Walker method. Add 1.6 mg to the weight of cuprous oxide (1.0 mg for ice cream). Refer both weights of copper to the Munson and Walker table 78, p. 564.

4. DETERMINATION OF THREE SUGARS IN A MIXTURE

(a) GENERAL

The analysis of mixtures containing three sugars requires the application of analytical processes which yield three equations. Special methods in great variety have been brought into use for the analysis of these complex products. The combinations of methods which have proved most successful are those which include at least one process which is selective for one of the constituent sugars. The number and nature of the possible combinations of methods is large, but for the present purpose it will suffice to illustrate the principles by a few examples given in detail.

In a very few instances one equation can be evaluated for total sugar in a mixture by using a physical method. Such a mixture can consist solely of pure sugars, but it is of such infrequent occurrence that the methods of analysis will not be described here. They can be found in Browne's Handbook of Sugar Analysis [3].

(b) THREE SUGARS BY COMBINATION OF POLARIMETRIC AND REDUCTION METHODS AND ONE SELECTIVE METHOD

Wherever this combination can be applied, it is the simplest method of analysis of a complex mixture, involving as it does but three stand-

ard operations. Thus for the analysis of a mixture of sucrose, dextrose, and levulose, a direct and invert polarization and a reducing-sugar analysis suffice for the completed determination.

The method is illustrated in the determination of the Browne polarizing constants [2]. It would seem preferable to call them "quotients" rather than "constants," since the value of the quotient is not constant but varies with the ratio of dextrose to levulose.

The Browne polarizing constants are defined by the expression $(S-P)/R$, in which S and R are the percentages of sucrose and reducing sugar, respectively, and P is the direct polarization. Assume a normal solution of a mixture of 99 percent of sucrose and 1 percent, or 0.26 g, of invert sugar. The invert sugar will rotate $-1.19\times0.26=-0.309$. The value of the quotient is then $99-(99-0.309)/1=0.309$. Similarly, if the reducing sugar were 1 percent levulose, the quotient would be 1.404, and if 1 percent dextrose, -0.806. At the ratio of dextrose to levulose of about 64 to 36, the quotient becomes 0.

To calculate the percentages of dextrose and levulose, Browne used the equations

$$x+ky=R$$
$$cx+c_1y+S=P,$$

in which x and y are the percentages of dextrose and levulose, respectively; k, the reducing ratio of levulose to dextrose; c, the polarizing ratio of dextrose to sucrose at 20° C; c_1, the polarizing ratio of levulose to sucrose; and R, the percentage of total reducing sugar, expressed as dextrose (Allihn method).

Solving the equations for x and y,

$$y=\text{percentage of levulose}=\frac{cR+S-P}{kc-c_1},$$

$$x=\text{percentage of dextrose}=R-ky.$$

Sucrose is estimated selectively by the Clerget method.

The numerical value of c is $52.74:66.5=0.793$; that of c_1, $-92.88:66.5=-1.397$. For k an average value of 0.915 is employed.

The method yields reliable results if the reducing-sugar content is not too low. If S approaches closely to P, small errors in either become large errors in their difference. It was, however, the only practicable method previous to the introduction of the selective method for levulose.

Zerban has shown the fair agreement of results obtained by this method with those obtained by two selective analyses. The comparative results are shown in table 30. The method of two selective analyses, combined with the determination of total reducing sugar, must be considered the more reliable procedure.

(c) THREE SUGARS BY COMBINATION OF TOTAL REDUCING POWER AND TWO SELECTIVE METHODS

Mixtures of sucrose, dextrose, and levulose can be analyzed by a selective determination of sucrose by the Clerget method, a selective determination of levulose by the Nyns method, and a determination of total reducing sugar. Alternatively, a selective determination of dextrose by the iodine-alkali reaction can be used to replace the levulose analysis, provided that adequate correction is applied for the action of iodine on the nonaldose sugars.

TABLE 30.—*Zerban analyses of dextrose and levulose in raw cane sugar*

Method I. Polarizing constants and total-reducing sugar

Method II. Total reducing sugar and selective levulose analysis

Sugar	Method I			Method II		
	R[1]	$D\%R$[2]	Pc[3]	R	$D\%R$	Pc[4]
SOME INDIVIDUAL SAMPLES						
	1.55	55.5	0.181	1.55	55.7	0.175
	0.73	47.5	.358	0.73	44.6	.425
	.88	51.5	.273	.88	51.0	273
	1.03	56.2	.166	1.03	54.8	.195
	0.94	65.7	−.043	0.94	59.1	.106
AVERAGE DEXTROSE-RATIO AND POLARIZING CONSTANTS						
Cuba	----------	49.7	0.305	----------	47.8	0.348
Puerto Rico	----------	53.7	.221	----------	51.9	.256
Santo Domingo	----------	45.8	.394	----------	49.7	.307
Hawaii	----------	48.9	.326	----------	48.0	.349
Philippines	----------	49.3	.317	----------	53.5	.224
ANALYSES OF TWO PAIRS OF SUGARS						
1, New crop	0.531	42.4	0.471	0.531	45.6	0.395
1, Old crop	1.245	63.1	.016	1.240	76.5	−.274
2, New crop	0.431	42.7	.464	0.430	50.2	.302
2, Old crop	.991	59.6	.091	.985	74.5	−.234

[1] Percentage of total reducing sugars found.
[2] Percentage ratio of dextrose to total reducing sugars.
[3] Polarizing constant.
[4] Polarizing constant calculated from dextrose and levulose found.

(1) SUCROSE, DEXTROSE, AND LEVULOSE IN RAW SUGAR.—Zerban and Wiley [20] have applied the method of two selective analyses to the determination of sucrose, dextrose, and levulose in raw cane sugar, using for levulose the modification of Jackson and Mathews and for sucrose the invertase Clerget analysis. For the determination of total reducing sugar they used the Lane and Eynon volumetric method, but since the original tables listed titers for dextrose, levulose, and invert sugar only, they prepared interpolated tables for varying ratios of these sugars in the presence of 10 and 25 g of sucrose, respectively. In abbreviated form, these data are reproduced in tables 90 and 91, p. 596. Zerban and Wiley found slightly higher factors for invert sugar than Lane and Eynon and recommend that the analyst verify the published factors or establish his own. A similar recommendation was made with respect to the Jackson-Mathews method. They found that in order to obtain the same copper equivalents as tabulated by these authors, they must conduct the reduction at 55.2° C instead of 55.0° C, as specified. They determined the reduced copper by ferric sulfate-permanganate titration.

The reducing power of dextrose (12.4 mg of dextrose=1 mg of levulose) determined by Jackson and Mathews was confirmed. Four grams of sucrose reduced 8.5 mg of copper; 5 g, 9.0 mg; and 2 g, 5.7 mg.

Procedure.—Transfer a sample of raw sugar containing 62.5 g of sucrose (determined by direct polarization) to a 250-ml flask, clarify with neutral lead acetate, make to volume, and filter. Delead with dry potassium oxalate. Determine (preferably in duplicate) apparent

levulose in 20-ml portions by the Jackson-Mathews procedure, p. 203, estimating copper by any desired method except that of direct weighing of the copper precipitate. Titrate the remainder of the solution against 10 ml of Soxhlet solution. If the titer is less than 15 ml, dilute 100 ml to 250 ml and repeat the titration. Determine the sucrose by the invertase Clerget analysis.

The calculation of results, made by successive approximation, is illustrated by an example. A sample, 64.60 g containing 62.5 g of sucrose, gave a Lane and Eynon titer of 18.13 ml which, estimated as invert sugar, indicated 239.4 mg of reducing sugars per 100 ml. By the Jackson-Mathews method, 76.9 mg of reduced copper was found; from which 9.0 mg is deducted to correct for the reducing action of 5 g of sucrose. By table 93, p. 597, 67.9 mg corresponds to 22.0 mg of apparent levulose in 20 ml of solution, or 110.0 mg in 100 ml.

	Mg
Total reducing sugars as invert	239.4
Apparent levulose, first approximation	110.0
Apparent dextrose, first approximation, 239.4−110.0	129.4
Equivalent levulose, 129.4÷12.4	10.4
Apparent levulose, second approximation, 110.0−10.4	99.6
Apparent dextrose, second approximation, 239.4−99.6	139.8
Equivalent levulose, 139.8÷12.4	11.3
Apparent levulose, third approximation, 110.0−11.3	98.7
Apparent dextrose, third approximation, 239.4−98.7	140.7

The levulose equivalent of the dextrose, 140.7÷12.4, is again 11.3, so that further approximation is unnecessary.

The ratio of levulose to dextrose is thus found to be 98.7 to 140.7, or 41 to 59. From table 90, p. 596, the factor is 43.3, and total reducing sugar, 238.8 in 100 ml. Calculated for original sample, levulose is 0.382 percent; dextrose, 0.542 percent; and total reducing sugar, 0.924 percent.

In a further study of raw-sugar analysis, Zerban [21] has compared the Browne method of polarizing constants with the method of total reducing sugar combined with selective methods for sucrose and levulose. He devised a less laborious method of calculation than that of successive approximations. Thus

$$ax+y=R \tag{57}$$

$$0.0806x+y=R_1, \tag{58}$$

in which x and y are the milligrams of dextrose and levulose, respectively, in 100 ml of solution analyzed; R is milligrams of total sugars, expressed as levulose by Lane and Eynon titration; and R_1, the milligrams of apparent levulose determined by the Jackson-Mathews method and corrected for the reducing effect of the sucrose. The factor, 0.0806, is the constant reducing ratio of dextrose to levulose, 12.4 mg of dextrose having the same reducing effect as 1 mg of levulose.

Solution of eq 57 and 58 gives

$$x=\text{mg of dextrose in 100 ml of solution}=\frac{R-R_1}{a-0.0806}$$

$$y=\text{mg of levulose in 100 ml of solution}=R-ax.$$

The calculation is facilitated by the factors in table 91, p. 596, which is abbreviated from the expanded form given in the reference cited. Interpolation yields the true factors accurately.

The simplified method of calculation is not as rigorous as the method of successive approximations, but the errors for small percentages of total sugars are within the error of experiment. For samples containing large amounts of reducing sugar in the presence of small amounts of sucrose, the successive approximation method is to be recommended.

The analytical procedure is described on page 227. Some typical analyses of individual samples are shown in table 30, p. 227. In table 30 are also given the averages of a large number of samples of different geographical origin. Interesting analyses were made of two pairs of samples produced from the same Cuban plantation in the crop year 1934. The *A* samples were manufactured in 1934, the *B* samples in 1935. In both cases the amount of total reducing sugars in the old-crop samples is more than twice that in the new crop, and at the same time the dextrose is very much higher. There is strong indication that the old-crop sugars have undergone inversion during storage and that levulose has been destroyed through the activity of torulas.

(2) Sucrose, Dextrose, and Levulose in Cane Molasses.—Erb and Zerban [22] extended the work of the New York Sugar Trade Laboratory to the determination of total reducing sugars, dextrose and levulose, in cane molasses. Total reducing sugars were determined by the Munson and Walker method in samples containing 0.4 g of total sugar. In amplification of the tables of Munson and Walker, they determined the copper value of sucrose mixed with pure dextrose and pure levulose, respectively, and also revised the tabulated values of sucrose–invert-sugar mixtures, deriving the formulas

$$D=0.38476\ \mathrm{CuO}+0.00009436\ \mathrm{CuO}^2-3.177,$$

$$L=0.4305\ \mathrm{CuO}+0.0000611\ \mathrm{CuO}^2-3.412,$$

$$I=0.40016\ \mathrm{CuO}+0.00009631\ \mathrm{CuO}^2-2.9911,$$

which are valid for 0.4 g of total sugar.

The revised values for invert sugar show, for concentrations of sugar above 150 mg., slightly higher weights of sugar than those of Munson and Walker for the same weights of copper.

For the analysis of molasses, total sugars were determined by the Munson and Walker method, as described above, and levulose was determined selectively in the same filtrate by the Jackson-Mathews procedure, page 203.

The experimental data were solved for the respective figures by substitution in the formulas

$$D=\frac{R_1-R_2}{a-0.081}$$

$$L=R_1-aD,$$

the sucrose having been determined previously by the Clerget method. R_1, total reducing sugars, expressed as levulose (table 92, p. 597), and R_2, the apparent levulose (table 93, p. 597), after deducting from the total copper precipitated the weight of copper reduced by the sucrose, p. 227.

These formulas are similar to those derived for the raw-sugar analysis, but the *a*'s now have different values because of the difference in method of total reducing-sugar analysis. The solution of these equations is greatly facilitated by use of the expanded table published by the authors. Here it is possible to include the table only in greatly abbreviated form, but interpolation yields correct figures for intermediate values of CuO.

(d) ANALYSIS OF A MIXTURE OF THREE SUGARS BY THREE REDUCTION PROCESSES

(1) STEINHOFF METHOD FOR DEXTROSE, MALTOSE, AND DEXTRIN [23].—Steinhoff has based a proposed method for the simultaneous determination of the three carbohydrates upon the assumption that all dextrins in starch-conversion products are nonreducing toward Fehling solution. In outline, he determined dextrose selectively by a modification of the Barfoed method, total reducing sugar by Fehling solution and total dextrose produced by complete hydrolysis of the mixture.

The required reagents consist of Soxhlet solutions I and II (p. 170), and III, a 50-percent sodium-acetate solution. Prepare also 0.1 *N* iodine and 0.1 *N* thiosulfate.

Weigh 8.75 g of commercial glucose sirup and make to 500 ml. (Solution *a*). For complete hydrolysis, transfer 50 ml to a 100-ml volumetric flask, add 25 ml of 3 *N* hydrochloric acid, and digest for 2½ hours in a boiling-water bath. Cool, neutralize with sodium hydroxide, and fill to mark. (Solution *b*). Reducing-sugar analysis is carried out in three 200-ml Erlenmeyer flasks.

Analysis A.—For selective dextrose analysis take 10 ml of Soxhlet solution I, 20 ml of solution III (sodium acetate), 10 ml of water, and 10 ml of solution *a*.

Analysis B.—For total dextrose and maltose, take 10 ml each of Soxhlet solutions I and II, 20 ml of water, and 10 ml of solution *a*.

Analysis C.—For total sugar in the hydrolyzed solution take 10 ml each of Soxhlet solutions I and II, 20 ml of water, and 10 ml of solution *b*. This aliquot sample contains half as much of the original sample as analyses *A* and *B*. Hence the dextrose observed is multiplied by 2 to correspond with that derived from a 175-mg aliquot.

All three flasks are brought to boiling and ebullition is continued for 2 minutes, or preferably allowed to stand in a boiling water bath for 20 minutes. Dissolve the cuprous oxide precipitate in hydrochloric acid, neutralizing the excess acid with sodium bicarbonate. Measure in an excess of 0.1 *N* iodine, and after cooling the solution, titrate the excess of iodine with thiosulfate. Calculate the number of milliliters of 0.1 *N* iodine consumed.

For the calculation of the results

$$\text{Percentage of dextrose}=\frac{100D}{W},$$

$$\text{Percentage of maltose}=\frac{100M}{W},$$

$$\text{Percentage of dextrin}=\frac{90(T-D-M)}{W},$$

in which D is the weight of dextrose found by analysis A when referred to column 1 of table 104, p. 609; M is the weight of maltose which corresponds to the milliliters of 0.1 N iodine which is obtained if the volume used in analysis A but calculated to Fehling solution by column 2 is deducted from the volume of iodine consumed in analysis B. T is the weight of total dextrose corresponding to the volume of iodine consumed in analysis C; and W is the weight in milligrams in the respective aliquot samples, that is, 175 mg.

Example.—8.75 g of a glucose sirup was analyzed as described above.

Analysis A.—9.17 ml of 0.1 N iodine was consumed. The aliquot contained 175 mg of the original sample. The 9.17 ml corresponds to 26.25 mg of dextrose.

$$\text{Dextrose}=\frac{100\times 26.25}{175}=15 \text{ percent.}$$

Analysis B.—16.60 ml of iodine was consumed. According to the table, 9.17 ml of iodine (analysis A) is equivalent to 8.24 ml when the analysis is carried out by the Soxhlet reagents. Hence, by deducting the reduction by dextrose, 16.60−8.24=8.36, we obtain the reduction caused by maltose. This volume of iodine corresponds to 45.5 mg of maltose by column 3

$$\text{Maltose}=\frac{100\times 45.5}{175}=26 \text{ percent.}$$

Analysis C.—21.56 ml of iodine was consumed by a sample half as great as in the preceding analysis. This corresponds, by column 4, to 72.82 mg of dextrose, which, multiplied by 2, equals 145.64 mg from a 175-mg sample. Deduct the dextrose and maltose already present before hydrolysis, that is, 26.25+45.5=71.75.

$$\text{Dextrin}=\frac{90\,(145.64-71.75)}{175}=38 \text{ percent.}$$

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XI. ANALYSIS OF SPECIAL PRODUCTS

1. HONEY [14]

(a) PREPARATION OF SAMPLE

(1) Liquid or Strained Honey.—If the sample is free from granulation, mix it thoroughly by stirring or shaking before weighing portions for the analytical determination. If the honey is granulated, place the container, having the stopper loose, in a water bath and heat at a temperature not exceeding 50° C, with occasional stirring until the sugar crystals dissolve. Mix thoroughly, cool, and weigh portions for the analytical determinations. If foreign matter, such as wax, sticks, bees, particles of comb, etc., is present, heat the sample to 40° C in a water bath and strain through cheesecloth in a hot-water funnel before weighing portions for analysis.

(2) Comb Honey.—Cut across the top of the comb, if sealed, and separate completely from the comb by straining through a 40-mesh sieve. When portions of the comb or wax pass through the sieve, heat the sample as in (1) and strain through cloth. If the honey is granulated in the comb, heat until the wax is liquefied; stir, cool, and remove the wax.

(b) MOISTURE

Proceed as directed under (c), page 262 of this circular.

(c) ASH

Weigh 5 to 10 g of honey into a platinum dish, add a few drops of pure olive oil to prevent spattering, heat carefully until swelling ceases, and ignite at a temperature not above dull redness until a white ash is obtained.

(d) DIRECT POLARIZATION—TENTATIVE

(1) Immediate Direct Polarization.—Transfer 26 g of the honey to a 100-ml flask with water, add 5 ml of alumina cream, dilute to the mark with water at 20° C, filter, and polarize immediately in a 200-mm tube.

(2) Constant Direct Polarization.—Complete the mutarotation by allowing the solution prepared for polarization to stand overnight before making the reading or by adding a few drops of NH_4OH to the solution before making to volume. If necessary to conserve the sample, the solution from the tube used in the immediate direct polarization (1) may be returned to the flask. Make the final reading at 20° C in a 200-mm tube.

(3) Mutarotation.—The difference between (1) and (2) is a measure of the mutarotation.

(4) Direct Polarization at 87° C.—Polarize the solution obtained under (2) at 87° C in a jacketed 200-mm metal tube, preferably of silver.

(e) INVERT POLARIZATION—TENTATIVE

(1) At 20° C.—Invert 50 ml of the solution obtained under (d), using either invertase or hydrochloric acid as directed on pages 157-58, or page 155 this Circular, and polarize at 20° C in a 200-mm tube.

(2) At 87° C.—Polarize the solution obtained under (1) at 87° C in a 200-mm tube.

(f) REDUCING SUGARS

Dilute 10 ml of the solution used for direct polarization (d) to 250 ml and determine reducing sugars in 25 ml of this solution by Lane-Eynon method, p. 185, or by the Munson-Walker method, p. 170, of this Circular. Calculate the result to percentage of invert sugar.

(g) SUCROSE

(a) Calculate from the data given in (d) (2) and (e) (1) if inversion is made by invertase, as directed on page 157. Use the formula given on page 158.

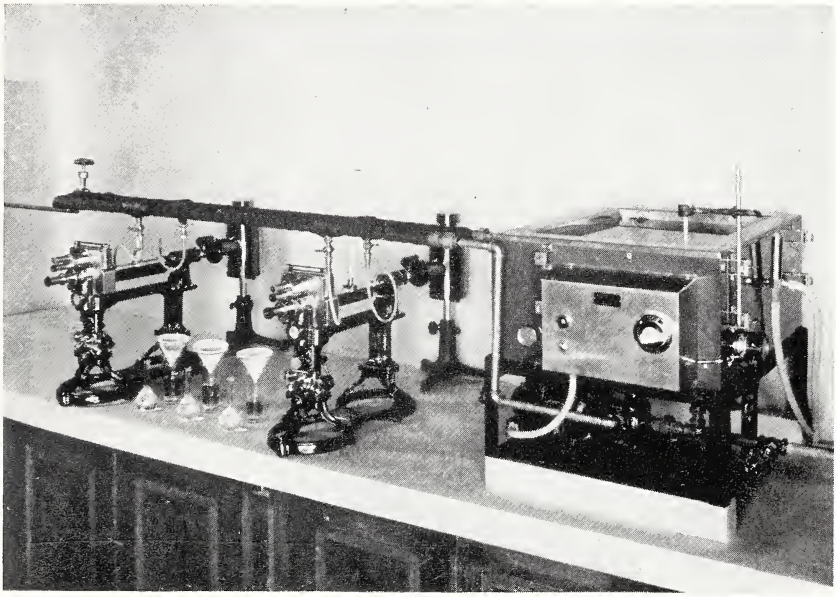

FIGURE 40.—*Apparatus for high-temperature polarization.*

(h) LEVULOSE—TENTATIVE

Multiply the direct reading at 87° C, (d) (4), by 1.0315, and subtract the product from the constant direct polarization at 20° C, (d) (2); divide the difference by 2.3919 to obtain grams of levulose in a normal weight of honey. From this figure calculate the percentage of levulose in the original sample.

(i) DEXTROSE—TENTATIVE

Multiply the percentage of levulose (h) by the factor 0.915, which gives its dextrose equivalent in copper-reducing power. Subtract the figure obtained from that of the reducing sugars (f), calculated as dextrose, to obtain the dextrose in the sample. Because of the difference in the reducing powers of the different sugars, the sum of the dextrose thus found and the levulose as obtained under (h) will be greater than the quantity of invert sugar obtained under (f).

(j) DEXTRIN (APPROXIMATE)—TENTATIVE

Using not more than 4 ml of water, transfer 8 g of the sample (4 g in the case of dark-colored honeydew honey) to a 100-ml flask by allowing the sample to drain from the weighing dish into the flask and then dissolving the residue in 2 ml of water. After adding this solution to the contents of the flask, rinse the weighing dish with two 1-ml portions of water, adding a few milliliters of absolute alcohol each time before decanting. Fill the flask to the mark with absolute alcohol, shaking constantly. Set the flask aside until the dextrin has collected on the sides and bottom and the liquid is clear. Decant the clear liquid through a filter paper, and wash the residue in the flask with 10 ml of 95-percent alcohol, pouring the washings through the same filter. Dissolve the dextrin in the flask with boiling water and filter through the filter paper already used, receiving the filtrate in a weighed dish prepared as directed on page 262, (c). Rinse the flask and wash the filter a number of times with small portions of hot water, evaporate on a water bath, and dry to constant weight at 70° C under a pressure of not more than 50 mm of mercury.

After determining the weight of the alcohol precipitate, dissolve the latter in water and make up to definite volume, using 50 ml of water for each 0.5 g of precipitate or part thereof.

Determine reducing sugars in the solution both before and after inversion by the method of Munson and Walker, p. 170, expressing the results as invert sugar. Calculate sucrose from the results thus obtained, and subtract the sum of the reducing sugars before inversion and sucrose from the weight of the total alcohol precipitate to obtain the weight of the dextrin.

(k) FREE ACID

Dissolve 10 g of the honey in water and titrate with 0.1 *N* NaOH solution, using phenolphthalein indicator. Express the results in terms of milliliters of 0.1 *N* NaOH required to neutralize 100 g of the sample.

(l) COMMERCIAL GLUCOSE

(1) Qualitative Test—Tentative.—Dilute the honey with water in the proportion of 1:1 and add a few milliliters of iodine solution (1 g of I, 3 g of KI, 50 ml of water). In the presence of commercial glucose the solution turns red or violet, the depth and character of the color depending upon the quality and nature of the glucose used. A blank test with a pure honey of about the same color should be made in order to secure an accurate color comparison. Should the honey be dark and the percentage of glucose very small, precipitate the dextrin that may be present by adding several volumes of 95-percent alcohol. Allow to stand until the precipitate settles (do not filter), decant the liquid, dissolve the residue of dextrins in hot water, cool, and apply the above test to this solution. A negative result is not proof of the absence of commercial glucose, as some glucose, especially of high conversion, does not give reaction with I. [2]

(2) Quantitative Method—Tentative.—An approximate determination can be made by Browne's formula as follows: Multiply the difference in the polarizations of the invert solution at 20° and 87° C, (e) (1) and (e) (2), p. 232, by 77, and divide this product by the percentage of invert sugar found in the sample after inversion. Mul-

tiply the quotient by 100 and divide the product by 26.7 to obtain the percentage of honey in the sample; 100 percent minus the percentage of honey gives the percentage of glucose. [2]

(m) COMMERCIAL INVERT SUGAR [3]

(1) Resorcinol Test [4]—Tentative.

a. Resorcinol solution.—Dissolve 1 g of resublimed resorcinol in 100 ml of HCl (sp gr 1.18 to 1.19).

b. Determination.—Introduce 10 ml of a 50-percent-honey solution into a test tube and add 5 ml of ether. Shake gently and allow to stand for some time until the ether layer is clear. Transfer 2 ml of this clear ether solution to a small test tube and add a large drop of the recently prepared resorcinol solution. Shake, and note the color immediately. A cherry-red color appearing at once indicates the presence of commercial invert sugar. Yellow to salmon shades have no significance.

(2) Aniline Chloride Test [5]—Tentative.

a. Reagent.—Aniline chloride solution.—To 100 ml of chemically pure aniline add 30 ml of 25-percent HCl.

b. Determination.—Introduce 5 g of the honey into a porcelain dish and add, while stirring, 2.5 ml of the recently prepared aniline reagent. In the presence of commercial invert sugar, the reagent assumes immediately an orange-red color turning dark red. Yellow to salmon shades have no significance.

The resorcinol test and the aniline-chloride test, when negative, may not be regarded as conclusive evidence of the absence of commercial invert-sugar sirup in honey.

(n) DIASTASE [6]—TENTATIVE

Mix 1 part of honey with 2 parts of sterile water. Treat 10 ml of this solution with 1 ml of 1-percent soluble starch solution and digest at 45° C for an hour. At the end of this time test the mixture with 1 ml of iodine solution (1 g of I, 2 g of KI, 300 ml of water). Treat another 10 ml portion of the honey solution, mixed with 1 ml of the soluble starch solution without heating to 45° C, with the reagent and compare the colors produced. If the original honey has not been heated sufficiently to destroy the diastase, an olive green or brown coloration will be produced in the mixture that has been heated at 45° C. Heated or artificial honey becomes blue.

2. MAPLE PRODUCTS [7, 14]

(a) PREPARATION OF SAMPLE

(1) Sirup.

For solids determination.—If the sample contains no sugar crystals or suspended matter, decant sufficient of the clear sirup for use in the determination. If sugar crystals are present, redissolve them by heating. If suspended matter is present, filter the sample through cotton wool.

For other determinations.—If sugar crystals are present, redissolve them by heating. If other sediment is present, distribute it evenly through the sirup by shaking. Transfer approximately 100 ml of the sirup, with its suspended sediment, to a casserole or beaker, add one-quarter the volume of water and evaporate over a flame. When the temperature of the boiling sirup approaches 104° C, draw a small

quantity into a thin-walled pipette of about 1-ml capacity, and cool to room temperature in running water. Wipe the outside of the pipette, allow the possibly diluted sirup in the point to escape, and make a refractometric measurement of the solids content of the cooled sirup. Repeat this procedure from time to time until a reading is obtained corresponding to 64.5-percent solids ($n_{20}=1.4521$), or to such other value as, in the experience of the analyst, will give a filtered sirup of 65.0-percent solids. Filter the sirup through a filter which will allow the 100 ml to pass within 5 minutes and adjust the filtrate to 65.0 ± 0.5-percent solids (refractometric) by thorough mixing with the appropriate quantity of water.

(2) Sugar and Other Solid and Semisolid Products—Tentative.

For moisture and solids determination.—Grind in a mortar, if necessary, and mix thoroughly.

For other determinations.—Prepare a sirup by dissolving approximately 100 g of the sample in 150 ml of hot water, boil until the temperature approaches 104° C and complete the preparation of the resulting sirup as directed under (1), commencing at "draw a small amount into a thin-walled pipette."

(b) MOISTURE OR SOLIDS

(1) Maple Sugar.—Proceed as directed under (b), p. 262.

(2) Maple Sirup, Maple Cream, Etc.—Proceed as directed under (c), p. 262, using a sample prepared as directed under (a) (1) p. 235. The determination may be made by means of the refractometer, as directed on page 258.

(c) ASH

Proceed as directed on page 264.

(d) POLARIZATION

(1) Direct Polarization.—Proceed as directed on page 157.

(2) Invert Polarization.

At 20° C.—Proceed as directed on page 155 or 157, after clarification with a minimum amount of basic lead acetate and the removal of the excess lead in the filtrate by anhydrous sodium carbonate.

At 87° C.—Polarize the solution obtained under (d) (1), at 87° C in a 200-mm tube.

(e) SUCROSE—POLARIMETRIC METHOD

Calculate from the results of (d) (1) and (d) (2), using the appropriate formula, page 156 or page 158.

(f) SUCROSE—CHEMICAL METHOD

By reducing sugars before and after inversion.—Determine the reducing sugars (clarification having been effected with neutral lead acetate, never with basic lead acetate) as directed on page 170, and calculate them to invert sugar from table 78, p. 564. Invert the solution as directed under (1), p. 156, exactly neutralize the acid, and again determine the reducing sugars, but calculate them to invert sugar from the table referred to above, using the invert column alone. Deduct the percentage of invert sugar obtained before inversion from

that obtained after inversion and multiply the difference by 0.95 to obtain the percntage of sucrose. The solutions should be diluted in both determinations so that not more than 240 mg of invert sugar is present in the aliquot taken for reduction. It is important that all lead be removed from the solution with anhydrous powdered potassium oxalate or Na_2CO_3 before reduction.

(g) REDUCING SUGARS AS INVERT SUGAR

(1) Before Inversion.—Proceed, as directed under 2 (a) (2), p. 170, on aliquots of the solution used for direct polarization, (d) (1), p. 236.

(2) After Inversion.—Proceed, as directed under (1), on aliquots of the solution used for invert polarization, (d) (2), p. 236.

(h) COMMERCIAL GLUCOSE [8]

(1) Substances Containing Little or No Invert Sugar.—Commercial glucose cannot be determined accurately owing to the varying quantities of dextrin, maltose, and dextrose present in the product. However, in sirups in which the quantity of invert sugas is so small as not to affect appreciably the result, commercial glucose may be estimated approximately by the following formula:

$$G=\frac{(a-S)100}{211},$$

in which

G=percentage of commercial glucose solids,
a=direct polarization, normal solution, and
S=percentage of cane sugar.

Express the results in terms of commercial glucose solids polarizing +211° S. (This result may be recalculated in terms of commercial glucose of any Baumé reading desired.)

(2) Substances Containing Invert Sugar.—Prepare an inverted half-normal solution of the substance as directed on page 156; cool the solution after inversion, make neutral to phenolphthalein with NaOH solution, slightly acidify with HCl (1+5) and treat with 5 to 10 ml of alumina cream before making up to the mark. Filter, and polarize at 87° C in a 200-mm jacketed tube. Multiply the reading by 200 and divide by the factor 196 to obtain the quantity of commercial glucose solids polarizing +211° V. (This result may be recalculated in terms of commercial glucose of any Baumé reading desired.)

(i) LEAD NUMBER

(1) Canadian Lead Number [9] (Fowler Modification).

Reagent—Standard basic lead acetate solution.—Activate litharge by heating it to 650 to 670° C for 2½ to 3 hours in a muffle. (The cooled product should be lemon color.) In a 500-ml Erlenmeyer flask provided with a return condenser, boil 80 g of normal Pb acetate crystals and 40 g of the freshly activated litharge with 250 g of water for 45 minutes. Cool, filter off any residue, and dilute with recently boiled water to a density of 1.25 at 20° C.

Determination.—Weigh the quantity of sirup containing 25 g of dry matter, transfer to a 100-ml flask, and make up to mark at 20° C, or use the solution in which the conductivity value has been determined

(j). Pipette 20 ml into a large test tube, add 2 ml of the standard basic Pb acetate solution, cork, and allow to stand for 2 hours.

Filter with suction on a 25-ml tared Gooch having an asbestos mat at least 3 mm thick. When nearly all the liquid has run through, fill the crucible with cold water. Repeat to a total of four washings, taking care to prevent formation of fissures in the precipitate by keeping it covered with water and avoiding too great suction. Dry at 100° C, weigh, and multiply the weight by 20.

(2) Winton Lead Number [10].

Reagent—Standard basic lead acetate solution.—To a measured volume of the reagent prepared for determination of the Canadian lead number (1) add 4 volumes of water, and filter. A blank should be run with each set of determinations.

Determination of lead in the blank.—Transfer 25 ml of the standard basic Pb acetate to a 100-ml flask, add a few drops of glacial acetic acid, and make up to the mark with water. Shake, and determine $PbSO_4$ in 10 ml of the solution, as directed below. The use of acetic acid is imperative in order to retain all Pb in solution when the reagent is diluted with water.

Determination.—Transfer 25 g of the sample to a 100-ml flask by means of water. Add 25 ml of the standard basic Pb acetate solution and shake. Fill to the mark, shake, and allow to stand for at least 3 hours before filtering. Pipette 10 ml of the clear filtrate into a 250-ml beaker, add 40 ml of water and 1 ml of H_2SO_4, shake, and add 100 ml of 95-percent alcohol, dry in a water oven, and ignite in a muffle or over a Bunsen burner, applying the heat gradually at first and avoiding a reducing flame. Cool and weigh. Subtract the weight of $PbSO_4$ so found from the weight of $PbSO_4$ found in the blank, and multiply by the factor 27.33. The use of this factor gives the Pb number directly, without the various calculations otherwise required.

(j) CONDUCTIVITY VALUE [11]

(1) Apparatus.

Conductivity cell.—Should be made of resistance glass with platinized Pt electrodes firmly fixed and adequately protected from displacement. These electrodes may be sealed in a vessel into which the solution under examination may be run and subsequently drawn off (Zerban type), or attached to a support so that they can be lowered into a cylinder (or a 100-ml beaker) containing the solution (dipping type). The cell must be provided with a thermometer graduated in tenths of a degree over the range 20 ° to 30 ° C, and the bulb must be placed in the immediate vicinity of the electrodes. The cell constant should be approximately 0.15.

Galvanometer or a microphone hummer (or an induction coil) and a sensitive telephone receiver.

Suitable source of current.—Dry or storage cells if a hummer or induction coil is used; 110-volt alternating current if a galvanometer is used.

Resistances of 10 and 100 ohms.—Should be fixed and accurate.

Slide wire or Wheatstone bridge.

Device for control of the temperature of the cell to within $\pm 0.1°$ *C.*—This may consist of a thermostat or a vessel into which water of suitable temperature may be run to adjust the cell contents to 25 ° C.

(2) Determination of the Cell Constant.—Prepare solutions of 0.3728 and 0.7456 g of dry KCl in water, which offers a resistance of at least 25,000 ohms in the cell, and make them to the mark at 20° to 25° C in 500-ml volumetric flasks. Fill the cell with the more dilute (0.01 *M*) solution, adjust to 25° ±0.1° C, measure the electrical resistance, and multiply the number of ohms by 141.2. Rinse with the stronger (0.02 *M*) solution, fill the cell with the solution, measure its resistance at 25° C, and multiply by 276.1. Average the two results.

(3) Determination.—Weigh out a quantity of sirup that contains 25 g of dry matter, transfer to a 100-ml volumetric flask with warm water of the same quality as that used in the determination of the cell constant, cool to 25° C, make to mark, and measure the resistance in the cell at 25° ±0.1° C. Divide the cell constant by the number of ohms found.

(k) MALIC-ACID VALUE (COWLES) [12]—TENTATIVE

Weigh 6.7 g of the sample into a 200-ml beaker; add 5 ml of water, then 2 ml of a 10-percent calcium acetate solution; and stir. Add, gradually and with constant stirring, 100 ml of 95-percent alcohol and agitate the solution until the precipitate settles, or let stand until the supernatant liquid is clear. Filter off the precipitate and wash with 75 ml of alcohol, 85 percent by volume. Dry the filter paper and ignite in a platinum dish. Add 10 ml of 0.1 *N* HCl, and warm gently until all of the lime dissolves. Cool, and titrate back with 0.1 *N* NaOH solution, using methyl orange indicator. The difference in milliliters divided by 10 represents the malic-acid value of the sample. Previous to use, the reagents should be tested by a blank determination and any necessary corrections applied.

3. DETERMINATION OF SUGARS IN MILK PRODUCTS

The estimation of lactose in fresh milk is, from the standpoint of sugar analysis, relatively simple, but the preparation of the sample for analysis involves procedures regarding which there is much dispute. The Association of Official Agricultural Chemists finds it satisfactory to clarify with copper sulfate in preparation for reducing-sugar analysis or with mercuric nitrate for polariscopic analysis. On the other hand, the British Subcommittee on Milk Products recommends the use of zinc ferrocyanide, prepared in the presence of the sample, but permits the use of phosphotungstic acid. The volume of the precipitate is relatively large and must be calculated or determined.

An important commodity is condensed milk sweetened with sucrose. Occasionally the sucrose is partially inverted by the action of enzymes or microorganisms, and in some instances further action of microorganisms converts the levulose so formed into a nonreducing levan. In some cases, other sugars may be added as sweetening agents. The analysis of such sugar mixtures becomes an intricate problem.

Many of the methods for the sugar mixtures in milk products have been elaborated solely for the purposes of milk analysis, but appear to be capable of general application to other products.

(a) DETERMINATION OF THE VOLUME OF THE PRECIPITATE

If the percentages of fat and protein of a milk product are known, the volume of the clarification precipitate can be calculated with fair approximation by the method of the British Subcommittee on Milk Products [13]. The volume of the protein precipitate varies with the nature of the precipitant. For phosphotungstic acid clarification the specific volume of fat is 1.08 and for protein, 0.74. The volume then is fat$\times$1.08+protein$\times$0.74, to which is added a further empirical correction of 1.5 ml.

For the zinc ferrocyanide method the volume of precipitate is about double that for the phosphotungstic acid precipitate. The volume of precipitate is then fat$\times$1.08+protein$\times$1.55. The British subcommittee, however, recommends actual determination of the volume of the precipitate for each sample [13].

(1) Weigh 100 g of milk into a 200-ml flask. Add precipitating reagents, make up to the mark at 20° C, filter, and polarize at 20° C. Reading=A.

(2) Weigh 100 g of the same milk and 16.8 g of sucrose into a 200-ml flask, dissolve the sugar, add precipitating reagents, make up to the mark at 20° C, filter, and polarize at 20° C. Reading=B.

(3) Weigh 140 g of the same milk into a 200-ml flask and add seven-fifths of the previous quantities of precipitating reagents. Make up to the mark at 20° C, and filter. Take 70 ml of the filtrate, make up to 100 ml, and polarize at 20° C. Reading=C.

(4) Measure 70 ml of the filtrate from (3) into a 100-ml flask, add 8.4 g of sucrose, dissolve, make up to the mark at 20° C, and polariez at 20° C. Reading=D.

The correction for volume of precipitate for 100 g of milk

$$=200\left(1-\frac{D-C}{13-A}\right)=\text{milliliters.}$$

(b) LACTOSE IN MILK [14]

(1) Optical Method.

Reagents.—(a) *Acid mercuric nitrate solution.*—Dissolve mercury in twice its weight of concentrated nitric acid and dilute with an equal volume of water.

(b) *Mercuric iodide solution.*—Dissolve 33.2 g of KI and 13.5 g of $HgCl_2$ in 200 ml of glacial acetic acid and 640 ml of water.

Determination.—Determine the specific gravity (20°/20°) of the milk and place in a flask graduated at 102.6 ml, the volume of milk indicated in table 31. Add 1 ml of solution (a) or 30 ml of solution (b), fill to the mark, shake frequently for at least 15 minutes, filter through a dry filter, and polarize. The volumes in the table are those of a double-normal weight of lactose (32.9 g per 100 ml); hence, if a 200-ml tube is used, divide the saccharimeter reading by 2 to obtain the percentage of lactose in the sample.

(2) Chemical Method.—Dilute 25 g of the sample with 400 ml of water in a 500-ml volumetric flask and add 10 ml of $CuSO_4$ solution (Soxhlet solution 1) and about 7.5 ml of a KOH solution of such strength that 1 volume is just sufficient to precipitate completely the copper as hydroxide from 1 volume of the copper sulfate solution. (Instead, 8.8 ml of 0.5 N NaOH solution may be used). After the addition of the alkali solution, the mixture must still have an acid reaction and con-

TABLE 31.—*Volume of milk corresponding to lactose double-normal weight*

Specific gravity (20°/20°)	Volume of milk for a lactose double-normal weight	Specific gravity (20°/20°)	Volume of milk for a lactose double-normal weight
	ml		*ml*
1.024	64.25	1.030	63.90
1.025	64.20	1.031	63.80
1.026	64.15	1.032	63.75
1.027	64.05	1.033	63.70
1.028	64.00	1.034	63.65
1.029	63.95	1.035	63.55
		1.036	63.50

tain copper in solution. Fill the flask to the 500-ml mark, mix, filter through a dry filter, and determine lactose in an aliquot of the filtrate by the Lane and Eynon or Munson and Walker method.

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XII. DETERMINATION OF PENTOSANS

1. DESCRIPTIVE

Pentosans are polysaccharides that yield pentoses upon hydrolysis. As their names imply, araban is thus related to arabinose, and xylan to xylose. The determination of pentosans depends upon their conversion into furfural and the subsequent determination of the furfural. The following reactions are assumed to take place:

$$\underset{\text{Pentosan}}{C_5H_8O_4} \xrightarrow{+H_5O} \underset{\text{Pentose}}{C_5H_{10}O_5} \xrightarrow{-3H_2O} \underset{\text{Furfural}}{C_5H_4O_2}$$

In carrying out pentosan determinations, one is therefore concerned with the quantitative conversion of the pentosan into furfural and the subsequent determination of the furfural.

The method universally adopted for converting pentosans into furfural consists in boiling the substance with 12-percent hydro-

chloric acid and collecting the distillate at the rate of 30 ml per 10 minutes. The quantity of distillate collected in some procedures is arbitrarily defined, while in others the distillation is continued until furfural ceases to come over, as indicated by the aniline acetate test.[11]

Methylfurfural gives only a faint-yellow color with aniline acetate. A solution of aniline in alcohol is used to test for this substance. Furfural and hydroxyfurfural derivatives are very sensitive to the aniline alcohol reagent, giving a bright-red color.

Jolles [1] employed steam distillation in order to remove the furfural from the acid solution more rapidly and reported quantitative conversion of arabinose and xylose into furfural. Pervier and Gortner [2] found that steam distillation from a 12-percent hydrochloric acid solution as used by Jolles, or from an 18- to 20-percent hydrochloric acid solution (the acid percentage being indicated by the boiling point), resulted in quantitative yields of furfural from arabinose and xylose. They also concluded that the rate of distillation did not affect the yield, and thus a slow current of steam was sufficient to sweep out the furfural as fast as it was formed from the pentose. When the usual method of distillation from 12-percent hydrochloric acid was used, these authors obtained a 95.3-percent yield of furfural from arabinose and 96.1-percent yield from xylose. These figures are approximately 7 percent higher than those generally obtained.

Kline and Acree [3] concluded that steam distillation gave no better yields of furfural from xylose than did the usual method of distillation.

Kullgren and Tydén [4] converted pentosans to furfural by distilling from a 13.15-percent hydrochloric acid solution saturated with sodium chloride. They thus had a constant acid concentration in the distilling flask.

Hughes and Acree [5] reported that a rapid steam distillation from a 12-percent hydrochloric acid solution saturated with sodium chloride gave quantitative yields of furfural from xylose as compared with 96-percent yields when a slow current of steam was used, irrespective of whether or not the solution was saturated with sodium chloride.

The gravimetric methods for the determination of furfural include the use of phloroglucin [6], barbituric acid [7], thiobarbituric acid [8], and diphenyl thiobarbituric acid [9]. The phloroglucin method has been carefully studied and generally adopted.

The volumetric methods include the use of phenylhydrazine [10], potassium bisulfite [1], and potassium bromate-bromide solution. The latter was studied by Pervier and Gortner [2]. They used an electrometric titration method and found that under their experimental conditions the potassium bromate and furfural reacted in the molecular ratio 1:3. Powell and Whittaker [11] determined the amount of bromine absorbed by a back-titration method, using potassium iodide and sodium thiosulfate. Under their experimental conditions they found that 4 atoms of bromine reacted with 1 molecule of furfural. In 1933, Magistad [12] pointed out that the furfural-bromate reaction is influenced greatly by temperature. Hughes and Acree [13] carried out the reaction at 0° C. By carefully controlling the temperature and time of reaction, they obtained reproduc-

[11] The aniline acetate reagent is prepared by shaking equal volumes of aniline and water in a test tube and adding glacial acetic acid until the solution is clear. Place a drop of the reagent on a filter paper and allow a drop of the distillate to spread into the reagent. If furfural is present, a red color will appear where the circles intersect. Toward the end of the distillation the red line will appear only after drying.

ible results in which 1 mole of bromine reacted with 1 mole of furfural. Kullgren and Tydén employed a potassium bromate-bromide solution, which they added at a temperature of 18° to 19° C, together with 10 ml. of ammonium molybdate. In 0 to 4 minutes a yellow color developed, and the reaction was allowed to run exactly 4 minutes after this coloration appeared. It will be noted that the bromine reaction with furfural takes place in two distinct stages. One mole of bromine reacts with furfural very rapidly and then another mole is slowly absorbed. Powell and Whittaker allowed their reaction mixture to stand 1 hour, under which condition more than 1 mole of bromine reacts with a mole of furfural.

During the distillation of plant products with hydrochloric acid, along with the furfural are formed other substances which react with phloroglucin and with potassium bromide-bromate. These include methylfurfural (from rhamnosan), hydroxymethylfurfural (from hexosans), and formaldehyde (from lignin). The separation of the phloroglucin compounds is dependent upon the assumption that furfural forms with phloroglucin, a product which is insoluble in alcohol, while the other phloroglucin compounds are soluble. This is not entirely true. The Kullgren process employs a second distillation, which destroys 33 percent of the methylfurfural and all of the hydroxymethylfurfural. Hughes and Acree [14] studied the reaction of bromine with furfural and methylfurfural at 0°C and found that by determining the amount of bromine consumed during two periods of time it was possible to calculate the quantities of furfural and methylfurfural present. They expressed the consumption of bromine at two periods of time, based upon the molar consumption of bromine for each aldehyde, by the following equations:

f=grams of furfural.
m=grams of methylfurfural.
x_1 and x_2=milliequivalents of bromine consumed by aliquots at times t_1 and t_2.
a_1 and a_2=molar consumption of bromine by furfural at t_1 and t_2.
b_1 and b_2=molar consumption of bromine by methylfurfural at t_1 and t_2.

$$m=(0.055)\frac{a_1x_2-a_2x_1}{a_1b_2-a_2b_1}$$

$$f=(0.048)\frac{b_2x_1-b_1x_2}{a_1b_2-a_2b_1}.$$

For 5- and 10-minute periods these equations become

$$m=(0.055)\frac{(1.00)(x_2)-(1.00)(x_1)}{(1.00)(1.63)-(1.00)(1.38)}.$$

$$f=(0.048)\frac{(1.63)(x_1)-(1.38)(x_2)}{(1.00)(1.63)-(1.00)(1.38)}.$$

2. STANDARD METHOD FOR THE ESTIMATION OF FURFURAL BY MEANS OF PHLOROGLUCIN

Reagents [6]—*Hydrochloric acid.*—Contains 12 percent by weight of hydrogen chloride. To 1 volume of concentrated hydrochloric

acid add 2 volumes of water. Determine the percentage of acid by titration against standard alkali and adjust to proper strength by dilution or addition of acid, as may be necessary.

Phloroglucin.—Dissolve a small quantity of phloroglucin in a few drops of acetic anhydride, heat almost to boiling, and add a few drops of sulfuric acid. A violet color indicates the presence of diresorcin. A phloroglucin which gives more than a faint coloration may be purified by the following method. Heat in a beaker about 300 ml of the dilute hydrochloric acid and 11 g of commercial phloroglucin, added in small quantities at a time, stirring constantly until it is nearly dissolved. Pour the hot solution into a sufficient quantity of the same hydrochloric acid (cold) to make the volume 1,500 ml. Allow to stand at least overnight, preferably several days, to permit the diresorcin to crystallize. Filter immediately before using. A yellow tint does not interfere with its usefulness. In using, add the volume containing the required quantity of phloroglucin to the distillate.

Determination.—Place such a quantity of the sample, 2 to 5 g, that the weight of phloroglucide obtained shall not exceed 0.300 g, in a 300-ml distillation flask, together with 100 ml of the dilute hydrochloric acid and several pieces of recently ignited pumice stone. Place the flask on a wire gauze, connect with a condenser, and heat, rather gently at first, and then regulating so as to distill over 30 ml in about 10 minutes. Pass the distillate through a small filter paper. Replace the 30 ml distilled by a like quantity of the dilute acid, added by means of a separatory funnel in such a manner as to wash down the particles adhering to the sides of the flask, and continue the process until the distillate amounts to 360 ml. To the total distillate add gradually a quantity of phloroglucin dissolved in the dilute hydrochloric acid and thoroughly stir the resulting mixture. (The quantity of phloroglucin used should be about double that of the furfural expected. The solution turns yellow, then green, and very soon there appears an amorphous greenish precipitate that grows darker rapidly, until it becomes almost black.) Make the solution up to 400 ml with the dilute hydrochloric acid and allow to stand overnight.

Collect the amorphous black precipitate in a weighed Gooch crucible having an asbestos mat, wash carefully with 150 ml of water so that the water is not entirely removed from the crucible until the very last, and dry for 4 hours at the temperature of boiling water. Cool, and weigh in a weighing bottle. The increase in weight is taken to be furfural phloroglucide. To calculate the furfural, pentoses, or pentosans from the phloroglucide, use the following formulas given by Kröber:

(1) For a weight of phloroglucide, designated by a in the following formulas, *under* 0.03 g:

$$\text{Furfural} = (a + 0.0052) \times 0.5170.$$
$$\text{Pentoses} = (a + 0.0052) \times 1.0170.$$
$$\text{Pentosans} = (a + 0.0052) \times 0.8949.$$

In the above and also in the following formulas, the factor 0.0052 represents the weight of the phloroglucide that remains dissolved in the 400 ml of acid solution.

(2) For a weight of phloroglucide *a between* 0.03 and 0.300 g, use Kröber's table (table 105, p. 610), or the following formulas:

$$\text{Furfural} = (a + 0.0052) \times 0.5185.$$
$$\text{Pentoses} = (a + 0.0052) \times 1.0075.$$
$$\text{Pentosans} = (a + 0.0052) \times 0.8866.$$

(3) For a weight of phloroglucide *a over* 0.300 g, use the following formulas:

$$\text{Furfural} = (a + 0.0052) \times 0.5180.$$
$$\text{Pentoses} = (a + 0.0052) \times 1.0026.$$
$$\text{Pentosans} = (a + 0.0052) \times 0.8824.$$

3. METHOD FOR THE ESTIMATION OF FURFURAL ACCORDING TO KULLGREN AND TYDÉN METHOD

Reagents.—Sodium hydroxide solution, 1.58 *N*.

A bromate-bromide solution containing 1.392 g of potassium bromate and 10 g of potassium bromide per liter, representing 0.05 *N* bromate solution.

Sodium thiosulfate solution, 0.05 *N*.

Ammonium molybdate solution containing 25 g of the salt per liter.

Hydrochloric acid (density, 1.065) which contains 13.15 percent of hydrochloric acid.

Sodium chloride and potassium iodide.

(a) PROCEDURE APPLICABLE TO THE DETERMINATION OF PENTOSANS OR METHYLPENTOSANS

Place a quantity of material corresponding to 0.15 to 0.2 g of xylose or rhamnose, or 0.20 to 0.30 g of arabinose, in a 300-ml distilling flask with 100 ml of 13.15-percent hydrochloric acid and 19 to 20 g of sodium chloride. Continue the distillation for 100 minutes for xylose and 140 minutes for arabinose and rhamnose at the rate of 25 ml per 10 minutes. After the distillation of each 25 ml add 25 ml of acid. For xylose 250 ml of distillate is obtained and for arabinose about 350 ml. Make the solution up to 250 ml in the first case, and 400 ml in the second, with hydrochloric acid. Place a 100-ml portion of this solution in a 500-ml flask fitted with a cork. While the liquid is cooling, add 200 ml of 1.58 *N* sodium hydroxide solution and cool to 18° to 19° C. Add at once 10 ml of ammonium molybdate solution and 25 ml of bromide-bromate solution. Place the flask over a white surface so as to be able to recognize the appearance of a yellow color. This usually occurs in zero to 2 minutes' time. Allow the flask to stand 4 minutes after the appearance of the yellow color, and add 1 g of solid potassium iodide and shake. Let stand for 5 to 10 minutes and titrate the liberated iodine with 0.05 *N* thiosulfate.

The bromate consumed is equal to the volume of solution added minus the volume of thiosulfate required. The total bromate is obtained by multiplying the volume of bromate consumed by 2.5 for xylose and by 4 for arabinose and rhamnose. Calling this volume *n* ml of 0.05 *N* potassium bromate, the quantities obtained in grams are

$$\text{Furfural} = n \times 0.00240.$$
$$\text{Xylose} = n \times 0.00425. \quad \text{Xylan} = n \times 0.00374.$$
$$\text{Arabinose} = n \times 0.00506. \quad \text{Araban} = n \times 0.00445.$$
$$\text{Rhamnose } (C_6H_{12}O_5.H_2O) = n \times 0.00346.$$

Rhamnosan $= n \times 0.00278$.
Pentosans (general) $= n \times 0.00410$.

To obtain the quantity of furfural in the original substance, increase the value obtained by 3.1 percent.

(b) ESTIMATION OF PENTOSES OR PENTOSANS IN THE PRESENCE OF HEXOSES AND POLYOSES

Take a quantity of substance that will give between 0.075 and 0.1 g of furfural. Carry out the distillation as described above. To the distillate add 2 ml (or 3 ml if the distillate reaches 350 ml) of hydrochloric acid (density, 1.19) and make up to 250 or 400 ml with 13.15-percent hydrochloric acid. Return 100 ml of this solution to the distillation flask, add 19 to 20 g of sodium chloride, and repeat the distillation with the addition of 25 ml of hydrochloric acid after each 25-ml distillation. When 100 ml has come over, neutralize and titrate as before. Calculate as before. As two distillations have been made, it is necessary to increase the furfural value by 3.1 percent twice when determining the amount of furfural produced by the original substance.

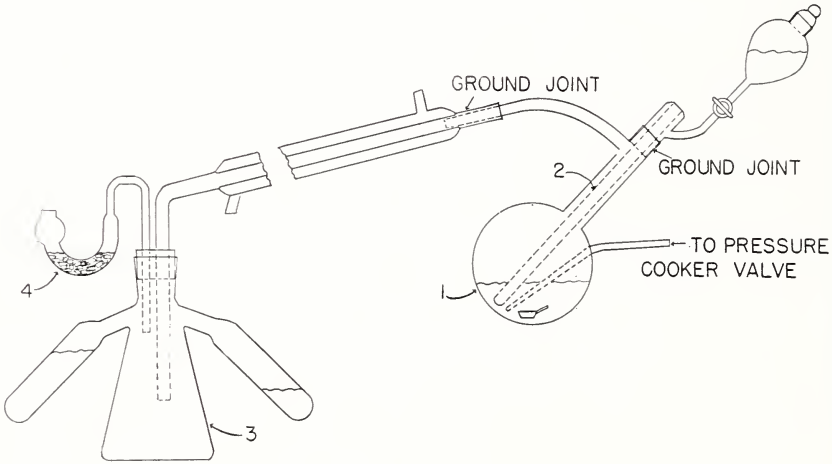

FIGURE 41.—*Steam-distillation apparatus used for furfural determinations.*
1, Distillation flask; 2, thermometer well; 3, titration flask; and 4, scrubber trap containing water and Raschrig Pyrex rings.

4. DISTILLATION AND VOLUMETRIC DETERMINATION OF FURFURAL FROM XYLOSE [5]

The xylose is weighed in a Pyrex micro pan and placed in flask 1 (fig. 41) along with 20 g of sodium chloride. The apparatus is then completely assembled. One hundred milliliters of 12-percent hydrochloric acid is added through the separatory funnel, and the temperature of the solution in the distilling flask is brought to 103° to 105° C. Steam at a pressure of 10 pounds per square inch (115° C) is then introduced at such a rate that with the distillation temperature at 110° $\pm 1°$ C, 200 ml of distillate is collected every 30 minutes. A constant level is maintained in the distillation flask by the addition of hydrochloric acid. The acidity of each fraction is determined by removing 1 ml and titrating it with 0.1 *N* sodium hydroxide (phenolphthalein).

This sample is then returned and the acidity of the distillate adjusted to about 1 *N*. The distillation is continued until the final fraction contains no furfural (aniline acetate test). The receiving flasks, in whose side arms have been previously placed the 0.1 *N* potassium bromate-bromide solution and the potassium iodide solution, are then placed in an ice bath to attain a temperature of 0° C. The potassium bromate-bromide solution is run in, thoroughly mixed, and allowed to react exactly 5 minutes, at which time the potassium iodide is added. The flask is removed from the ice bath and shaken vigorously to allow all of the free bromine to react. The contents of the flask are then titrated with 0.1 *N* sodium thiosulfate in the presence of starch indicator. Under these conditions 1 mole of bromine reacts with 1 mole of furfural; hence 1 ml of 0.1 *N* potassium bromate is equivalent to 0.0048 g of furfural.

A representative analysis is indicated by the following: 0.1600 g of xylose, 11 fractions of 200 ml, and 21.33 ml total volume of potassium bromate-bromide solution consumed. The authors were interested in obtaining 100-percent yields, and thus have used precautions not required when an error of 1 to 2 percent could be tolerated.

With a 25-mg sample of furfural it was found that 2 percent was collected in the trap. When rubber stoppers were used to close the distilling flask, an error of 0.04 to 0.06 ml of 0.1 *N* potassium bromate-bromide resulted for each 200 ml of distillate. The potassium bromate-bromide and the potassium iodide solutions may be cooled in separate containers, the bromate solution being quantitatively washed into the flask before the thiosulfate titration. The distillate may be collected in one flask and an aliquot part used for the final titration. This method has also been applied to rhamnose and arabinose [15].

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XIII. DENSIMETRY

1. GENERAL

Density is the term used to represent the mass per unit volume and is expressed in grams per milliliter; thus $d=(m/v)$, in which d is the density, m the mass, and v the volume of the substance. Since

1 ml of distilled water at 4° C, the temperature of its maximum density, (d=1.00000) weighs 1 g in vacuo, densities are usually referred to water at 4° C. The standard temperature adopted for sugar analysis is 20° C, and density measurements are usually made at this temperature. The density of a sugar solution at 20° C referred to water at 4° C is indicated as follows: $d_{4°}^{20°}$. Unless otherwise stated, densities refer to weights reduced to vacuo and are termed "true" or "absolute" densities.

The term "specific gravity" is used to express the relative masses of equal volumes of the substance in question and water, each substance being at a definitely stated temperature. For example, specific gravity at $d_{20°}^{20°}$ means the specific gravity of the substance at 20° C referred to water at 20° C as unity. Specific gravity is frequently referred to as relative density.

2. DEGREES BRIX (OR BALLING)

The system of graduating hydrometers on the basis of the percentage by weights of sucrose in a pure sucrose solution was first devised by Balling [1]. The Balling scale was subsequently recalculated by Brix [2], and the instrument is now generally referred to as the Brix hydrometer, and the readings are indicated by the term "degrees Brix." The original hydrometers were calibrated at 17.5° C, but at present most Brix hydrometers are standard at 20° C.

3. DEGREES BAUMÉ

The Baumé hydrometer is widely used in the sugar industry, particularly in connection with the sale of molasses and sirups. The original instrument was devised by Antoine Baumé [3], a French chemist, in 1768. Baumé described his method of graduating the hydrometer in L'Avant Coureur in 1768 and repeated them in the several editions of his Elements de Pharmacie. In the eighth edition of this work, published in Paris in 1797, he stated that he constructed his instrument in this way:

> For the hydrometer for liquids heavier than water he prepared a solution of salt containing 15 parts of salt by weight in 85 parts of water by weight. He described the salt as "very pure" and "very dry" and stated that the experiments were made in a cellar in which the temperature was 10° Réaumur (12.5° C). The zero on the scale indicated the point to which the instrument sunk in distilled water and the 15-mark the point to which it sunk in the 15-percent salt solution.
>
> With a pair of dividers the space between 0 and 15 was divided into 15 equal parts, and degrees of the same size were continued above 15.

Although the degrees on the Baumé scale are entirely arbitrary and bear no obvious relation to the density of the liquid, the instrument met with speedy acceptance by workers in the sugar as well as other industries. With the general use of the Baumé scale, other investigators found difficulty in following the original directions for calibrating the instrument, and the values of the scale divisions have been variously reported. This led to the introduction of a number of different so-called Baumé scales.

Chandler, [4] in a paper read before the National Academy of Sciences at Philadelphia in 1881, gave an admirable review of the origin and history of the Baumé scales in use up to that time. He gave the details of 23 different scales for liquids heavier than water. This subject of Baumé scales is also discussed in Bureau Circular C59.

In view of the uncertainty which existed because of the number of different scales, Bates and Bearce [5] devised a new Baumé scale for sugar solutions. This has three features that commend it for use in sugar work.

1. It is based upon the density values of Plato, which are considered the most reliable.
2. It is standard at 20° C, the most widely accepted temperature for sugar work.
3. It is based on the modulus 145, which has already been adopted by the Manufacturing Chemists Association of the United States, by the National Bureau of Standards, and by all American manufacturers of hydrometers.

In constructing this table, Bates and Bearce reduced the Plato density values $d_{4°}^{20°}$ to specific gravities at 20°/20° C in order that zero degrees Baumé correspond to zero percentage of sucrose and zero degrees Brix.

The relation between specific gravity 20°/20° C and degrees Baumé (Bates and Bearce) is as follows:

$$\text{Degrees Baumé} = 145 - \frac{145}{\text{sp gr } 20°/20° \text{ C}}.$$

The Bates and Bearce table of equivalents is now in general use; table 109, p. 614.

4. DETERMINATION OF DENSITY

(a) BY MEANS OF HYDROMETERS

Hydrometers are seldom used for great accuracy, since the usual conditions under which they are used preclude such special manipulation and exact observation as are necessary to obtain high precision. It is, nevertheless, important that they be accurately graduated to avoid, as far as possible, the necessity for instrumental corrections. To obtain this end, it is necessary to employ certain precautious and methods in standardizing these instruments.

The hydrometer should be clean, dry, and at the temperature of the liquid before immersing.

The liquid in which the observation is made should be contained in a clear, smooth, glass vessel of suitable size and shape.

In order that a hydrometer may correctly indicate the density of a specified liquid, it is essential that the liquid be uniform throughout and at the standard temperature.

To insure uniformity in the liquid, stirring is required shortly before making the observation.

In making the determination, the hydrometer is slowly lowered into the liquid slightly beyond the point where it floats naturally and then is allowed to float freely.

The scale reading should not be made until the liquid and hydrometer are free from air bubbles and at rest.

In reading the hydrometer scale, the eye is placed slightly below the plane of the surface of the test liquid; it is raised slowly until the surface, seen as an ellipse, becomes a straight line. The point where this line cuts the hydrometer scale should be taken as the reading of the hydrometer.

The liquid should be at nearly the temperature of the surrounding air, as otherwise its temperature will change during the observation, causing not only differences in density but also doubt as to the actual temperature. When the temperature of observation differs from the standard temperature of the instrument the observed reading differs from the normal reading by an amount depending on the difference in temperature and on the relative thermal expansions of the instrument and the particular liquid. If the latter properties are known, tables of corrections for temperature may be prepared for use with hydrometers at various temperatures. Such tables should be used with caution, and only for approximate results when the temperature differs much from the standard temperature or from the temperature of the surrounding air. Such temperature corrections are given in tables 110 and 111, pp. 624-25. Further information on the use and testing of hydrometers is given in Bureau Circular C16, The Testing of Hydrometers.

In case the sample is too dense for direct determination, the following dilution method of the AOAC [6] may be employed.

Dilute a weighed portion with a weighed quantity of water or dissolve a weighed portion and dilute to a known volume with water. In the first instance, the percentage of total solids is calculated by the following formula:

Percentage of solids in the undiluted material$=WS/w$, in which

S=percentage of solids in the diluted material,
W=weight of the diluted material, and
w=weight of the sample taken for dilution.

When the dilution is made to a definite volume, the following formula is to be used:

Percentage of solids in the undiluted material$=VDS/w$, in which

V=volume of the diluted solution,
D=specific gravity of the diluted solution,
S=percentage of solids in the diluted solution, and
w=weight of the sample taken for dilution.

A table for the comparison of density, degrees Brix, and degrees Baumé, etc., is given in table 109, p. 614.

In applying the dilution method to low-grade products, such as final molasses, the results obtained are higher than when direct methods are used. This is due to the fact that when diluted with water the solutions of the dissolved salts and other impurities contract by amounts different from solutions of pure sucrose.

(b) BY MEANS OF PICNOMETERS

(1) General.—For more accurate determinations of the density of liquid sugar products, such as sirups and molasses, some form of picnometer or specific gravity bottle is used. The procedure is as follows: Carefully clean the picnometer by filling with a solution of potassium dichromate in concentrated sulfuric acid, allowing to stand for several hours, emptying, thoroughly washing with water, and, finally rinsing with alcohol. Dry the instrument in an air bath, cool and weigh. Fill the picnometer with recently boiled distilled water which has previously been cooled to 18° or 19° C, insert the stopper or thermometer, being careful to prevent the introduction of air bubbles,

and place the filled instrument in a water thermostat held at 20° C. Allow to remain in the thermostat for a sufficient time to reach the temperature of 20° C. Adjust the volume by removing the excess water which has exuded from the capillary stem, fit the ground-glass cap in place, and remove the instrument from the bath; wipe dry with a clean cloth and after allowing to stand for 15 to 20 minutes, weigh.

Reduce the weight in air of the contained water to the weight in vacuo. Obtain the volume of the picnometer by dividing the weight in vacuo of the water content by the density of water at 20° C, 0.9982343. After emptying and drying the picnometer, fill it with the sample in question, and ascertain the weight of the contained sample at 20° C. Reduce the weight in air of the contained sample to the weight in vacuo. Divide the weight of contained sample in vacuo by the volume of the picnometer to obtain the true density, $d_{4°}^{20°}$.

(2) Method of Newkirk.—The accurate determination of the density of blackstrap molasses is difficult due to the high viscosity of the material and to the presence of included and dissolved gases. Newkirk [7] has designed a special picnometer for making the determination (fig. 42). It consists of a bottle, *C*, fitted with an enlargement at the top, *B*, ground optically flat and closed by another optical flat, *A*. An expansion chamber, *D*, is ground to the bottle and fitted with a vacuum connection, *E*. To avoid loss of water due to evaporation under reduced pressure, the connecting tube is fitted with a stopcock, *F*, so that when the proper vacuum has been reached the apparatus can be closed off from the vacuum source. In using the picnometer, the expansion chamber, after lubrication of all joints with molasses, is placed on the bottle. The molasses to be analyzed is allowed to flow into the bottle and into the expansion chamber until the latter is about one-third full. The vacuum line is then connected and the pressure reduced until the gas expands into visible bubbles. The apparatus is then closed off by turning the stopcock, *F*, and the whole placed in a thermostat and allowed to remain until the temperature has reached equilibrium and all of the bubbles have collected in the expansion chamber. The expansion chamber is removed and the volume fixed by carefully sliding plate *A* over surface *B*. The picnometer is then removed from the thermostat, wiped clean, placed in the balance case, and weighed. The weight of the contained sample is corrected to vacuo and compared with the weight of an equal volume of water at 4° C in vacuo.

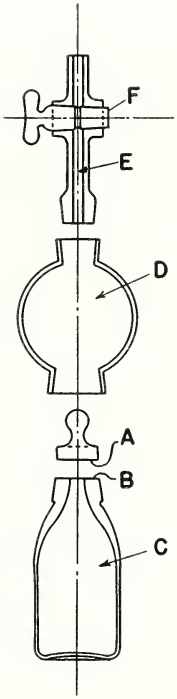

Figure 42.—*Newkirk picnometer.*

(3) Weight per Gallon of Molasses.—Since, in commercial transactions, molasses is sold both by volume and by weight, the determination of the weight per gallon is of considerable importance. The method employed at the National Bureau of Standards and adopted by the United States Customs Service is as follows:

A special 100-ml calibrated volumetric flask with a neck of approximately 8 mm inside diameter shall be used. Weigh the flask empty and then fill it with molasses, using a long-stem funnel reaching below the graduation mark, until the level of the molasses reaches the lower end of the neck of the flask. The flow of molasses may be stopped by inserting a glass rod of suitable size into the funnel so as to close the stem opening. Remove the funnel carefully to prevent the molasses coming in contact with the neck, and weigh flask and molasses. Add water almost up to the graduation mark, running it down the side of the neck to prevent mixing with the molasses. Allow to stand several hours or overnight to permit the escape of bubbles. Place the flask in a constant temperature water bath at 20° C for a sufficient time for it to reach the temperature of the bath, then make to volume at that temperature, with water. Weigh. Reduce the weight of the molasses to vacuo and calculate the density.

Example.

Weight per gallon determined at 20° C.
Weight of flask, 37.907 g.
Weight of flask and molasses, 167.148 g.
Weight of flask, molasses, and water, 174.711 g.

167.148 g − 37.907 g = 129.241 g = weight of molasses (in air with brass weights).
174.711 g − 167.148 g = 7.563 g = weight of water (in air with brass weights).
Calculating volume of water from weights in air at 20° C.
Divide weight of water in air by weight of 1 ml of water in air at 20° C (table 106, p. 612), 7.563/0.99718 = 7.584 ml.

Volume of flask at 20° C, 100. 060 ml
7. 584 ml
———
92. 476 ml = volume of molasses.

To reduce weight of molasses to vacuo:
129.241/8. 4 = 15.4 ml = volume of brass weights.

(8.4 = density of brass weights).
92.5 ml = volume of molasses (approximate).
15.4 ml = volume of weights.
———
77.1 ml = net volume of air displaced.

77.1 × 0.0012 = 0.093 g, buoyancy correction to be added to weight of molasses. (0.0012 g = weight of 1 ml of air at 760 mm at 20° C).

129. 241
0. 093
———
129. 334 = weight of molasses in a vacuum.

$$d_{4^\circ}^{20^\circ} = \frac{129.334}{92.476} = 1.3986.$$

By interpolation from table 117, p. 644,
Weight per gallon in air at 20° C = 11.664 pounds.

(c) BY MEANS OF DIRECT-READING BALANCE

The weight per gallon of molasses may be determined directly by means of a torsion balance designed by H. J. Bastone, of the American Sugar Refining Co. It is fitted with two beams, one a double beam for taring the sample bottle, and the other a recording beam graduated in pounds per gallon from 10.80 to 12.05 in 1/100 pound per

gallon. A bottle or picnometer for containing the molasses is furnished with the balance. The performance of the balance has been investigated by Snyder and Hammond [8], who deemed it more convenient and accurate to fix the volume by sliding a flat glass disk seated on the flat polished top of the perforated stopper. Johnson and Adams [9] and Newkirk [7] have shown the accuracy of thus fixing the volume. By this procedure only a very thin film of molasses remained between the disk and the top of the stopper. The calibration of the volume of the bottle and the direct determinations were made in the same manner.

This balance seems entirely satisfactory for most determinations of the weight per gallon of molasses, provided the usual precautions are taken to allow the foam to subside and occluded gases to escape. Any direct-reading balance will be found useful in commercial work and routine testing as compared with other methods, since results may be obtained without resort to tedious calculations.

(d) BY MEANS OF ANALYTICAL BALANCE

Another method of determining the specific gravity of sugar solutions is based on the well-known principle of Archimedes that a body immersed in a liquid is buoyed up by a force equal to the weight of the displaced liquid. In making a determination, a glass sinker or bulb weighted with mercury is suspended from the arm of a balance by means of a fine platinum wire. It is weighed in air, immersed in distilled water, and immersed in the sugar solution. The specific gravity is calculated from the equation

$$S=\frac{A-C}{A-B},$$

where

S=specific gravity of sugar solution,
A=weight of sinker in air,
B=weight of sinker in distilled water,
C=weight of sinker in sugar solution.

By reducing the weights in air to weights in vacuum and taking into account the temperature, the density of the air, and the atmospheric pressure, the true density may be calculated.

The so-called Westphal balance employs the same principle as the above and is so graduated that the specific gravity is obtained directly from the readings of the riders on the beam. A more detailed discussion may be found in textbooks on physics.

5. DENSITY OF SUCROSE SOLUTIONS

The density of sucrose solutions of different concentrations has been the subject of extensive study by investigators over a period of many years. Among the early workers in the field were Balling [1], Niemann [10], Brix [2], Gerlach [11], Scheibler [12], and others. A number of tables were published, varying with respect to the temperature, and expressed in terms of true density or of specific gravity. In 1900 the German Normal-Aichungs-Kommission published density tables of sucrose solutions [13] based on the very precise determinations of

F. Plato in collaboration with J. Domke and H. Harting. These tables include the percentages of sucrose by weight for density at 20°/4° C, table 113, p. 626, and specific gravities 15° C/15° C and t° C/15° C. These tables are considered the most accurate available and are universally accepted as standards. Using the Plato tables as a basis, numerous other tables have been computed, giving such values as grams of sucrose per 100 g of solution (Brix), grams of sucrose per 100 ml of solution, etc. Among the more widely used of these are the tables of Sidersky, Les densités des solutions sucrees á differentes temperatures, Paris, 1908.

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XIV. REFRACTOMETRY

1. GENERAL

The refractive index of a pure sucrose solution is an accurate measure of the concentration of dissolved substance. The first refractometer table appears to have been prepared by Ströhmer [1], who showed the relation between the refractive index and the specific gravity of sugar solutions. Stolle [2] determined the refractive indices of solutions of sucrose, dextrose, levulose, and lactose, using the Pulfrich refractometer. He found but little variation in the refractive index of solutions of the different sugars at the same concentration.

Tolman and Smith [3], using an Abbe refractometer, found that solutions of a number of sugars and related substances in equal percentage composition by weight gave approximately the same refractive index. They recommended the use of the refractometer in the determination of soluble carbohydrates in solution and pointed out the advantages of the method from the standpoint of speed, ease of manipulation, and the small amount of sample required.

To expand the usefulness of the refractometer, Geerligs [4] showed that the refractive indices of impure sugar solutions, even when the impurities consisted of mineral salts, yielded far more reliable measures of total dissolved substance than the determinations by densimetric measurement.

Hugh Main [5] prepared a table of refractive indices of sucrose solutions and demonstrated the applicability of the Abbe refractometer in sugarhouse work. Schönrock [6], using methods of high precision, determined the indices of sucrose solutions for concentra-

tions ranging from 0 to 66 percent. Landt [7] redetermined the indices for concentrations from 0 to 24 percent and obtained values in almost perfect agreement with the Schönrock values for that range.

In 1936 the International Commission for Uniform Methods of Sugar Analysis, realizing the need for a standard table of refractive indices of sugar solutions, adopted such a table [8]. This table, known as the "International Scale (1936) of Refractive Indices of Sucrose Solutions at 20° C," is constructed from the values of Schönrock-Landt (1933) up to 24 percent, of Schönrock (1911) from 24 to 66 percent, and of Main from 71 to 85 percent. The values 67 to 71 were obtained by extrapolation of the Schönrock values as a straight-line curve to meet the Main value at 71. This table in an expanded form is given in table 122, p. 652.

A similar table, based on the same data for use with the tropical model refractometer, standard at 28° C, is given in table 124, p. 658. Temperature corrections are made by means of tables 123 and 125.

2. PRINCIPLES OF THE ABBE REFRACTOMETER

When a ray of light travels through a homogeneous medium, its path is a straight line. However, when the ray passes from one medium to another at an angle oblique to the surface of separation of the two media, the direction of the ray changes abruptly at the surface of separation. In addition to the portion of the ray which penetrates the second medium and is bent or refracted, a portion of the light is reflected. According to Snell's Law, the sine of the angle of refraction bears a constant ratio to the sine of the angle of incidence for all angles of incidence, the value of the ratio depending on the nature of the two media at the surface of separation at which the refraction takes place, and also on the wave length of the incident light. This law is usually expressed as

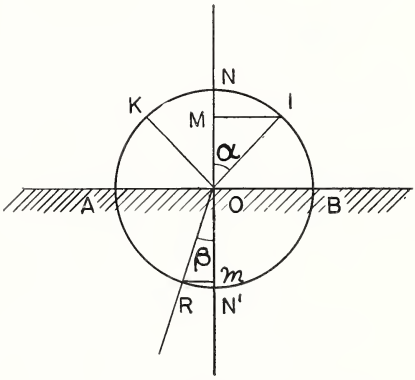

FIGURE 43.—*Refraction of light.*

$$n=\frac{\sin i}{\sin r}, \tag{59}$$

where n is the index of refraction; i, the angle of incidence; and r, the angle of refraction. This is illustrated by figure 43.

Suppose AB represents the surface of separation between two media, say, air above and water below, and that a ray of light having the direction IO is incident to AB at O. Let NON' be the normal to the surface of separation, AB. A portion of the light of the ray IO is reflected in the direction OK; the other portion is refracted in the direction OR. The angle IOM, or α, is the angle of incidence, and angle ROm, or β, is the angle of refraction.

In sugar analysis two types of refractometers are generally used, the Abbe and the immersion. In both of these the method of grazing incidence is employed. If light passes from a rarer to a denser medium, the angle of refraction will be smaller than the angle of incidence. The largest angle of incidence is 90°, and therefore there will be a maximum angle of refraction (less than 90°). This angle is called the critical angle. Equation 59 then becomes

$$n=\frac{1}{\sin rc}, \tag{60}$$

where rc is the critical angle.

In the Abbe refractometer, instead of actually reading the value of the critical angle in degrees and minutes and computing the index by means of a formula, the sector scale of the instrument is graduated directly in refractive indices, the intervals of which have been computed for the constants of the glass of the Abbe prisms. In making a determination with the instrument, the high-index prism is rotated about an axis perpendicular to the axis of the observing telescope until the border line of total reflection coincides with the intersection of the cross hairs of the telescope. Attached to the prism is an alidade with index, which moves along the graduated sector scale as the prism is rotated, permitting the reading of the index.

In the immersion refractometer the objective lens of the telescope forms an image of the border line between the light and dark portions of the field on a scale engraved on the plane side of the collecting lens in the eyepiece.

In both the Abbe and the immersion refractometer, compensators are provided to permit the use of white-light illumination. In the Abbe instrument two Amici prisms, which rotate in opposite directions, compensate for the combined dispersion of the sample and prism and produce a sharp image of the dividing line. These compensating prisms furnish a means of measuring the dispersion.

(a) DISPERSION

The dispersion of a substance, (n_D-1/n_F-n_C) may be calculated from the amount of rotation of the compensator prisms with respect to one another. n_D, n_F, and n_C are the indices of the substance for the sodium line, the blue hydrogen line, and the red hydrogen line, respectively. By means of a drum on which is engraved an arbitrary scale, one of the Amici compensating prisms is rotated until the border line is achromatized and the scale reading taken. Suitable charts or tables are furnished by the manufacturers to facilitate conversion of the scale readings to values for the dispersion.

(b) EFFECT OF TEMPERATURE

Both the refractive index and the dispersion vary with change of temperature. For liquids the temperature coefficients generally are larger and negative. It is therefore essential that the temperature be known and be kept constant during observation. Most Abbe refractometers are provided with water-jacketed prisms, which permit the circulation of water at a constant temperature. These instruments are also fitted with suitable thermometers for indicating the temperature of the material and the prisms.

(c) ILLUMINATION

The refractometer may be illuminated by daylight. It has been found more satisfactory, however, to use an incandescent electric lamp of suitable intensity, provided with a shield to eliminate the disturbing influence of extraneous light.

(d) ADJUSTMENT OF THE INSTRUMENT

In many laboratories, the scale of the Abbe refractometer is frequently checked for adjustment, a practice which should be generally

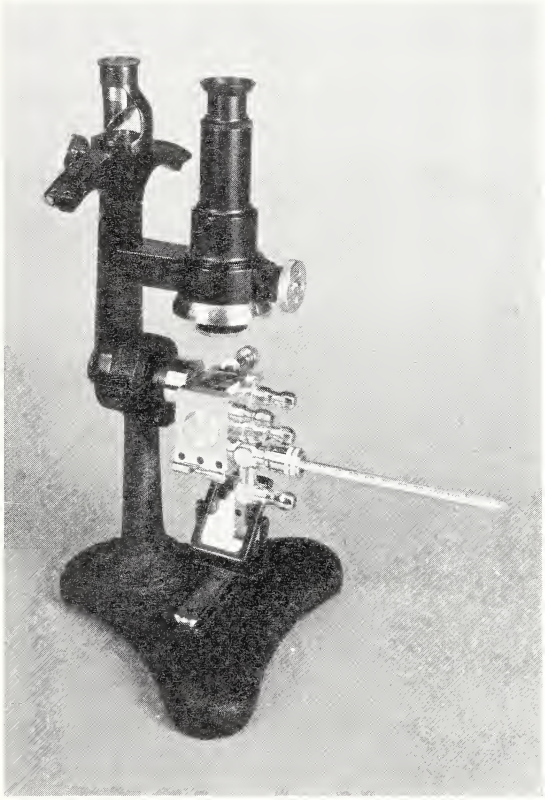

FIGURE 44.—*Abbe refractometer.*

followed. Most instruments are furnished with a test plate made of special glass and whose index has been carefully measured and the value engraved on it. The test plate is applied to the upper prism with the polished end toward the light source, by means of a drop of monobromnapthalene. A series of careful readings is then taken, and the average value thus obtained is compared with the value engraved on the test plate. If necessary, the correction may be made by turning a small screw in the telescope tube, which moves the objective, causing the dividing line to shift.

(e) METHOD OF DETERMINING REFRACTIVE INDEX

Place a few drops of the solution on the polished face of the fixed prism and slowly bring the two prisms together and clamp them. To insure a sharp, clear image use sufficient liquid to fill the space between the prisms. Swing the instrument to an upright position and adjust the illuminating mirror so that the light source is reflected into the lower prism of the instrument. Rotate the compensating prisms to obtain a sharp colorless dividing line. Circulate water at a constant temperature, preferably 20° C, through the jackets of the prisms long enough to allow the temperature of the prisms and of the sample to reach an equilibrium, continuing the circulation during observations and taking care that constant temperature is maintained. If the determination is made at a temperature other than 20° C, correct the reading to the standard temperature of 20° C by means of tables 123 or 127, pp. 657, 664.

Caution must be observed if the humidity causes condensation of moisture on the exposed faces of the prisms. If such a condition exists, make the measurements at room temperature and correct the readings to 20° C by means of table 123 or 126.

Dark-colored solutions, such as molasses, are frequently difficult or even impossible to read on the refractometer. In such cases it is necessary to follow the procedure of Tischtschenko [9], who diluted the dark-colored solution with a pure sucrose solution of about the same concentration. Water should never be used, since such dilution introduces errors due to contraction in volume. The method employed is as follows:

Mix thoroughly a weighed quantity of the solution under examination (A) and a weighed quantity of a solution of pure sucrose of about the same concentration (B) whose sugar content has been previously determined by the refractometer. Obtain the refractive index of this mixture and, by means of table 122, p. 652, convert to percentage of dry substance. The percentage of dry substance in the sample in question is calculated by the formula:

$$X=\frac{(A+B)\ C-BD}{A}, \tag{61}$$

where

X=percentage of dry substance to be found,
A=weight in grams of the sample mixed with B,
B=weight in grams of pure sucrose solution used in the dilution,
C=percentage of dry substance in the mixture $A+B$ obtained from the refractive index,
D=Percentage of dry substance in the pure sucrose solution obtained from its refractive index.

In using the refractometer for determining the percentage of dry substance in solution, it is well to consider the effect of impurities, such as salts and organic nonsugars. Tolman and Smith [3] and others have shown that the instrument is applicable for determining the soluble carbohydrates in solution. The various sugars have approximately the same refractive index for equal concentrations. Stanek [10] has shown the effect of organic salts of sodium and potassium on the refractometric estimation of dissolved solids.

3. IMMERSION REFRACTOMETER

This instrument is designed for the measurement of solutions in bulk, but, with accessory prisms, may be used where only small quantities of solution are available.

Originally the immersion instrument of Zeiss [11] was designed with a single prism having a range of refractive indices from 1.32 to 1.36. The present design permits the use of interchangeable prisms, usually six in number, extending the range to 1.54. The arbitrary scale of the instrument, graduated in equal divisions from −5 to +105, is engraved on the plane side of the collecting lens of the

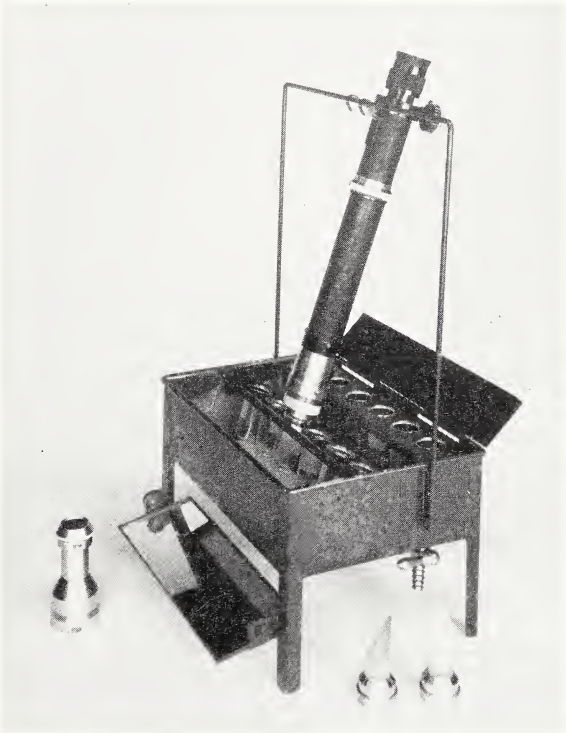

FIGURE 45.—*Immersion refractometer.*

eyepiece. The image of the border line is coincident with the scale. By means of the micrometer drum, readings may be made to tenths of a scale division. Each instrument is furnished with tables for converting the readings on the arbitrary scale to refractive indices. Since the relation between the arbitrary scales and refractive indices is not the same for all immersion refractometers, it is necessary to make the conversons by means of the tables furnished with the individual instrument.

The refractive indices corresponding to the scale divisions of the original single prism Zeiss immersion refractometer are given in table 32.

TABLE 32.—*Refractive indices corresponding to the scale divisions of the original Zeiss immersion refractometer*

Scale reading	Refractive index	Scale reading	Refractive index
−5	1.32539	55	1.34836
0	1.32736	60	1.35021
+5	1.32932	65	1.35205
10	1.33126	70	1.35388
15	1.33320	75	1.35569
20	1.33513	80	1.35750
25	1.33705	85	1.35930
30	1.33896	90	1.36109
35	1.34086	95	1.36287
40	1.34275	100	1.36464
45	1.34463	105	1.36640
50	1.34650		

In the Bausch & Lomb immersion refractometer the six interchangeable prisms were furnished and have the following index ranges:

A, 1.32539 to 1.36639.
B, 1.36428 to 1.40608.
C, 1.39860 to 1.43830.
D, 1.43620 to 1.47562.
E, 1.47320 to 1.51335.
F, 1.50969 to 1.54409.

The adjustment of the scale of the instrument is made for each prism by means of a test solution or test plate.

With prism *A* the adjustment is made with distilled water; *B*, with a standard sodium chloride solution; *C*, with a test piece of fluorite; and *D*, *E*, and *F*, with glass test pieces.

The observations regarding illumination and temperature control of the Abbe refractometer also apply to the immersion instrument.

The use of the immersion refractometer has been found advantageous by Bachler,[12],who devised a "one-solution method of analysis of sugar products," in which a sufficient quantity of a normal weight solution of the product is prepared and all or part of the necessary analytical data are obtained on this one solution. Certain changes were necessary in the immersion refractometer. At the suggestion of Bachler, the firm of Carl Zeiss, of Jena, produced an immersion refractometer with a single prism having a range of from n_D 1.331 to 1.372 and adjusted with distilled water at scale division 0. With the use of this instrument and the Goldbach flow-through cell, the method has been shown to give satisfactory results for factory control work.

4. SPECIAL REFRACTOMETERS

For special purposes there are available other types of refractometers. A pocket-type instrument is used for the estimation of the sugar present in the juice of the cane. Another special type is the factory refractometer, which is mounted on the vacuum pan and permits readings to be taken during the boiling process.

A new type of laboratory instrument is now in the course of manufacture by the Bausch & Lomb Optical Co. It is mounted in a horizontal position and illuminated by a sodium lamp. It combines features of both the Abbe and the immersion instruments and is capable of readings to a few units in the fifth decimal place.

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XV. DETERMINATION OF MOISTURE

1. GENERAL

An accurate determination of the moisture in sugar products is frequently a matter of great difficulty, and the proper procedure has not been definitely established. Moist sugar or sugar products, sirups, and molasses resist drying with great obstinacy. Sometimes the material is hygroscopic. At ordinary pressures, moisture can be removed only by prolonged heating at a high temperature. But a high temperature frequently exerts a destructive effect on the solid sugars. The destructive action of a temperature of 100° C. is a particularly important consideration in the case of levulose and, to a less extent, in the cases of dextrose and sucrose. Consequently, the best drying methods are those which combine mild temperature and high vacuum. If the substance is in the form of a sirup, drying is facilitated by mixing it thoroughly with dry quartz sand or pumice. The action of the sand is to cause a larger area to be exposed and prevent the formation of a crust. Flaked asbestos or, for fluid substances, a roll of filter paper may be used.

Below are given various methods in common use for determining dry substance. The method to be adopted depends somewhat upon the material. If levulose is present in considerable quantity, the temperature of drying should not exceed 70° C.

2. METHOD OF THE UNITED STATES BUREAU OF CUSTOMS

For control analysis of raw sugars, the Bureau of Customs, Treasury Department, has adopted an arbitrary method which yields readily reproducible results. The procedure is as follows [1]: For the determination of moisture in sugars, dry approximately 4 g in a metal dish 55 mm in diameter and 15 mm in height. Subject each sample to a temperature of 100° C. for 2 hours, care being exercised that the dishes are not in close proximity to the heaters.

In making the determination, dishes of polished aluminum with tightly fitting covers are used. Upon removing from the drying oven, the dish is immediately covered and placed in a desiccator. As soon as the dishes and contents have cooled, they are weighed. The loss of weight is expressed as moisture.

3. METHODS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS

(a) DIRECT DRYING [2]

(Applicable to Cane and Beet Raw and Refined Sugar)

Dry 2 to 5 g of the prepared sample in a flat dish (Ni, Pt, or Al), at the temperature of boiling water, for 10 hours; cool in a desiccator and weigh. Dry again for an hour or until the change in weight is not more than 2 mg. For sugars of large grain, heat at 105° to 110° C to expel the last traces of occluded water. Report the loss as moisture.

(b) VACUUM DRYING [3]

Dry 2 to 5 g of the prepared sample in a flat dish (Ni, Pt, or Al, and with a tightly fitting cover) at a temperature not exceeding 70° C (preferably at 60° C), under a pressure not exceeding 50 mm of Hg, and for 2 hours. Remove from the oven, put cover in place, cool in desiccator, and weigh. Redry for an hour and repeat until the change in weight is not more than 2 mg between successive weighings at 1-hour intervals. The oven should be bled with a current of dry air during drying to insure removal of water vapors.

(c) DRYING ON QUARTZ SAND [2]

(Applicable to massecuites, molasses, and other liquid and semiliquid products)

Digest pure quartz sand that will pass a 40-mesh but not a 60-mesh sieve with hydrochloric acid, wash free from acid, dry, and ignite. Preserve in a stoppered bottle. Place 25 to 30 g of the prepared sand and a short stirring rod in a dish approximately 55 mm in diameter and 40 mm in depth, fitted with a cover. Dry thoroughly, cover dish, cool in a desiccator, and weigh immediately. Then add sufficient diluted sample of known weight to yield approximately 1 g of dry matter and mix thoroughly with the sand. Heat on a steam bath for 15 to 20 minutes and stir at intervals of 2 to 3 minutes, or until the mass becomes too stiff to manipulate readily. Dry at 70° C under a pressure of not to exceed 50 mm of mercury. Make trial weighings at 2-hour intervals toward the end of the drying period (about 18 hours) until the change in weight does not exceed 2 mg.

For materials containing no levulose or other readily decomposable substance, the material may be dried at atmospheric pressure by heating 8 to 10 hours in a water oven at the temperature of boiling water. The sample is cooled in a desiccator and weighed; the heating and weighing are repeated until the loss in 1 hour does not exceed 2 mg. The loss of weight is reported as moisture.

(Dry sand, as well as the dried sample, will absorb an appreciable quantity of moisture after standing over most desiccating agents, therefore all weighings should be made as quickly as possible after cooling in the desiccator.)

4. ADDITIONAL METHODS

The length of time required to determine moisture in molasses and other low-grade products by drying on sand has led to the introduction of a number of special methods, such as the method of Spencer

[4] and the method of Rice and Boleracki [5]. In the Spencer method the drying is effected in a specially designed electric oven. The method is applicable to solid sugars as well as liquid sugar products. The samples are placed in aluminum capsules fitted with metallic gauze bottoms which permit free passage of air. When liquid or semiliquid products are to be dried, the sample is absorbed on asbestos [6]. Air, heated by passing over an electric heating element, is passed through the sample and the moist air is continuously withdrawn by suction.

The Rice and Boleracki method [5] consists in spreading a very thin film of molasses or sirup on thin sheets of silver and drying in a vacuum oven at 70° C. In the hands of an experienced operator the method appears to yield concordant results and has the added advantage of rapidity. It is necessary to exercise some care in preparing the film for drying and also in the manipulation during drying and weighing. The authors recommend the method for the determination of moisture in such products as honey, invert sirup, and blackstrap molasses.

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XVI. DETERMINATION OF ASH

Although the determination of ash in sugars and sugar products is subject to considerable uncertainty, it is still widely used as an indication of the mineral constituents present. In routine analysis the socalled "sulfated-ash" method is employed, largely on account of its simplicity and reproducibility. In this method any volatile constituents, such as Cl, NO_3, CO_2, etc., are driven off and are replaced by SO_4. This replacement is considered advantageous in that it compensates for the losses. A further advantage is the conversion of volatile salts, such as KCl, into the nonvolatile sulfate. The method is as follows:

1. SULFATE METHOD

Weigh 2 to 5 g of the sample in a 50- to 100-ml platinum dish, add 0.5 ml of concentrated H_2SO_4 or 1.0 ml of 1:1 H_2SO_4, heat gently on a hot plate until the sample is well carbonized, and then heat in a muffle furnace at a low red heat until all carbon is burned. Cool and add a few drops more of H_2SO_4, heat until this is fully volatilized, then cool in desicator and weigh. Reignite in the muffle furnace to constant weight. Express the result as the percentage of sulfated ash.

The general practice in many laboratories is to deduct one-tenth of the amount of sulfate ash to reduce to the normal ash. This deduction of 10 percent has been studied by many investigators and found to be in error for cane products. Jamison and Withrow [1] found that the value for sulfate ash in Cuban raw sugar, even with the customary 10-percent correction, was about 34 percent higher than the ash by

direct incineration. Ogilvie and Lindfield [2] found the correction factor to be from 12 to 15 percent for beet sugars and from 6 to 26 percent for cane sugars.

Jamison and Withrow proposed a modification of the sulfate method, in which they added 2 ml of sulfuric acid (2:1) to the sample of sugar, heated the sample on a hot plate until completely carbonized, and finally ignited it in the muffle furnace to a white ash. After cooling the ash, they added 3 or 4 drops of sulfuric acid (2:1) and heated it until the excess acid was driven off. They again ignited the ash in the muffle for 15 minutes.

2. METHODS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS [3]

In addition to the sulfate-ash method, the AOAC has adopted as official two methods for carbonated ash, as follows:

Method I.—Heat 5 to 10 g of the sample in a 50- to 100-ml platinum dish at 100° C until the H_2O is expelled, add a few drops of pure olive oil, and heat slowly over a flame until swelling ceases. Then place the dish in a muffle and heat at low redness until a white ash is obtained. Treat the residue with a little $(NH_4)_2CO_3$ solution, reevaporate, and heat again in the muffle at a very dull red heat to constant weight.*

Method II.—Carbonize 5 to 10 g of the sample in a 50- to 100-ml platinum dish at a low heat and treat the charred mass with hot water to dissolve the soluble salts. (In low-purity products the addition of a few drops of pure olive oil may be desirable.) Filter through an ashless filter, ignite filter and residue to a white ash, add the filtrate of soluble salts, evaporate to dryness and ignite to about 525° C to constant weight.*

3. ADDITIONAL METHODS

A number of other methods of determining ash have been proposed by various investigators, the details of some of which have been collected by Jamison and Withrow [1]. The methods are as follows:

Oxalic acid method of Grobert [4].

Quartz sand modification of Alberti and Hempel [5].

Benzoic acid modification of Boyer [6].

Zinc oxide modification [7].

Lixiviation modification [8].

Von Lippman advocates taking the dried-out sample on which the water determination has been made, saturating it with vaseline oil (having a boiling point of about 400° C), and igniting the mixture. The carbonized mass is then to be burned to ash in a mixed current of air and oxygen.

Since certain insoluble materials, such as sand and clay, which may be present in the sugar, and would therefore be included in the ash as determined by incineration, have no appreciable effect on the sugar in the process of refining, it is frequently necessary to determine the percentage of soluble ash. This may be accomplished by dissolving the sugar in hot water, filtering, washing the filter thoroughly with hot water, and evaporating the combined filtrate and washings in a platinum dish to dryness. The ash in the dry residue is then determined by one of the standard methods.

*The use of $(NH_4)_2CO_3$ was dropped in 1940.

The determination of ash by means of conductivity measurements is treated in chapter XVII, p. 275.

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XVII. ELECTRICAL CONDUCTANCE OF SUGAR SOLUTIONS

1. INTRODUCTION

Since the electrical conductance of a liquid may be made a measure of the concentration and mobility of conducting particles in solution, its measurement is useful in determining these qualities in sugar products. It has been used extensively, principally as a rapid method of estimating the ash content of solutions [1, 2, 3] at various stages of manufacture in order to predict their performance in subsequent stages or as an index of the quality of the finished product. Many have found, however, that it is not always necessary to convert the conductance measurement to the more familiar value of sulfate or carbonate ash. In such cases, conductance values are reported in units of specific conductance.

More recently, conductance measurements have come into use in the sugar-manufacturing process to control such operations as boiling [4], crystallization [5], centrifuging [6], and others [7], and in the laboratory to determine purity [8, 9] and concentration of solute [10].

Briefly, electrical conductance is the reciprocal of electrical resistance. In sugar solutions it is expressed in units of specific conductance or reciprocals of units of specific resistance, which in turn may be defined as the resistance in ohms of a column of liquid 1 cm long and having a uniform cross-sectional area of 1 cm^2.

To determine the specific conductance of any volume of liquid containing an electrolyte, it is therefore necessary to measure (a) the resistance in ohms of the liquid, and (b) the dimensions of the volume of liquid causing this resistance. This measurement may be performed with great precision, provided errors depending on the temperature of the solution, the construction of the bridge, oscillator, balancing capacitor, resistance standards, and change of apparent resistance with frequency, have been eliminated or corrected [11, 12].

The resistance of the solution is determined by connecting the cell, Z_x, figure 46, in one arm of an alternating-current bridge and adjusting R_v and C_v until no current flows between the points C and D, as detected by means of head phones, T. Then, if Z_1 and Z_2 are electrically the same, the value of R_v may be used to determine the resistance of the column of solution in the cell.

The volume of liquid causing this resistance is most conveniently measured indirectly as explained later under the section on Conductivity Cells, p. 268.

The possibility of electrolysis and oxidation-reduction in sugar solution has dictated the use of alternating current for the measurement of electrical conductance. Although alternating current does tend to reverse the effects of electrolysis, this reversal is not complete except under special conditions. Furthermore, the use of alternating current has introduced complicated electrical phenomena in the bridge network. The conductivity cell, being a part of this network, behaves in a manner that can be approximately simulated by a circuit made up of resistors and capacitors [12, 44]. The resistance of the column of liquid in the cell can be balanced by the variable resistor,

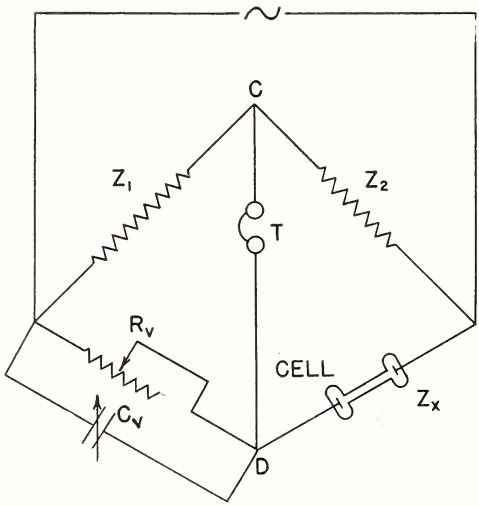

FIGURE 46.—*Direct-reading bridge circuit for electrical conductance.*

R_v, figure 46, and the capacitance is most conveniently balanced by the variable capacitor, C_v, placed in parallel with the variable resistor. There still remains, however, a residual effect, which will be referred to as electrode-polarization reactance. The magnitude of this effect, which tends to increase the apparent resistance of the solution, is influenced by the degree of platinization, the material of the electrodes, the composition of the electrolytes, and the frequency of the alternating current [12, 17].

2. APPARATUS

(a) BRIDGE

Most of the bridge circuits of recent design for studies of sugars are modifications of the type used by Kohlrausch [13], figure 47. The most important change, aside from improvements in apparatus, is that the majority read directly either in ohms or ash percentage.

The Sandera bridge [14], figure 48, although basically a Wheatstone

bridge, depends not on the variation of resistance to accomplish balance but on the variation of the distance between electrodes. The cell, C, and the calibration resistor, R, which remains unchanged during any one measurement, form two arms of the bridge. The other two arms are incandescent lamps, L_1 and L_2. These lamps are arranged in such a manner that light falls on opposite sides of an opaque wedge, P. The bridge is balanced by modifying the distance between the electrodes of the cell until the light reflected from the wedge is of equal intensity on both sides. After proper adjustment, the distance between the electrodes indicates ash percentage.

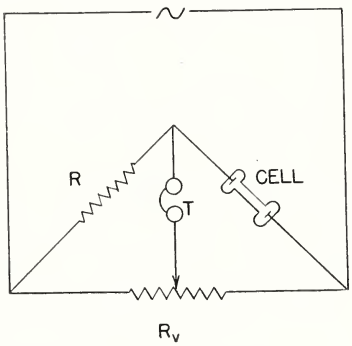

FIGURE 47.—*Kohlrausch bridge circuit for electrical conductance.*
R, fixed resistance; R_v, balancing resistance; T, headphones.

(b) NULL-POINT INDICATOR

In most precision bridges, a telephone receiver, sensitive to the frequency of the alternating current flowing through the bridge, is connected as shown in figure 46 to indicate the absence of current across CD when both the resistance and capacitance branches are balanced.

An electron-ray tube (6E5) has been successfully employed in a bridge circuit as a visual null-point indicator. This circuit, figure 49, may be used at any frequency between 1,000 and 15,000 cycles, and if the tuned circuit, L_1 and C_{13}, is properly selected, it is sensitive to a change in cell resistance of 1 part in 100,000, with a potential difference of less than 2 volts between the bridge terminals, A and B, figure 46.

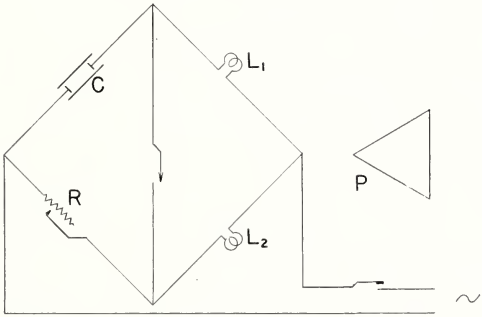

FIGURE 48.—*Sandera bridge circuit.*

Other types of indicators are those which are sensitive to frequencies of 60 cycles or lower, as, for example, an alternating-current galvanometer, milliameter, etc. Such types are particularly useful when observations must be made in noisy surroundings. However, the polarization reactance resulting from these low frequencies must be ignored or compensated for in the manner described under Checking Cells, p. 274

(c) OSCILLATOR

Since the electrolytes in sugar solutions are usually of unknown composition and may affect the electrode polarization reactance in a different manner in different solutions, it is best to reduce this effect as much as possible by using electrodes coated with platinum or palladium black, and employing a frequency of at least 1,000 cycles per second. For extreme precision, measurements should be made at two or more frequencies and values so found should be extrapolated to infinite frequency [12, 15].

The most useful source of current to accomplish this is obtained by using a variable-type vacuum-tube oscillator. With this source, the frequency may be varied and errors due to bridge or cell design thus can be detected and often eliminated.

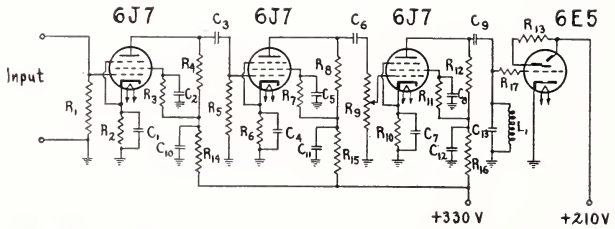

FIGURE 49.—*Wiring diagram of electrical conductance bridge null-point indicator.*

The human ear has a practically constant sensitivity at frequencies between 1,000 and 5,000 cycles. The oscillator should, therefore, be capable of supplying a current at any desired frequency between these limits if a telephone receiver is to be used as an indicator. In order to increase the precision of bridge setting, the oscillating current should have a pure sine wave form or be reasonably free from overtones, for if the bridge is balanced at the fundamental frequency and there remain notes of other frequencies in the detector branch of the bridge network, the sharpness of setting will be diminished and the time required to find the minimum will be increased. Since the current flowing through the cell heats the solution, and a potential difference between electrodes above 1.23 volts changes the bridge balance [12, 16, 44], the intensity and time of current flow should be reduced as much as possible.

(d) CONDUCTIVITY CELL

Since the conductance of a sugar solution is expressed in units of reciprocals of resistance and specific resistance has been defined as the resistance of a column of substance 1 cm long and 1 cm^2 in cross-sectional area, the specific resistance of any other column of the substance may be found from the equation

$$\rho = R \div \frac{l}{a} \tag{62}$$

or, since $k = 1/\rho$, the specific conductance may be found by equation

$$k = \frac{1}{R} \times \frac{l}{a}, \tag{63}$$

where R is the resistance in ohms; ρ, the resistivity or specific resistance; k, the specific conductance; l, the length in centimeters; and a, the uniform cross-sectional area in square centimeters. The values of l and a are usually combined and expressed as one quantity, l/a, which is defined as the "cell constant." The cell constant is best determined by measuring, in the cell to be calibrated, the resistance of a standard solution of known specific conductance, k, substituting in eq 63, and solving for l/a. As shown later, page 275, these constants should be based on the resistance extrapolated for infinite frequency [12, 16].

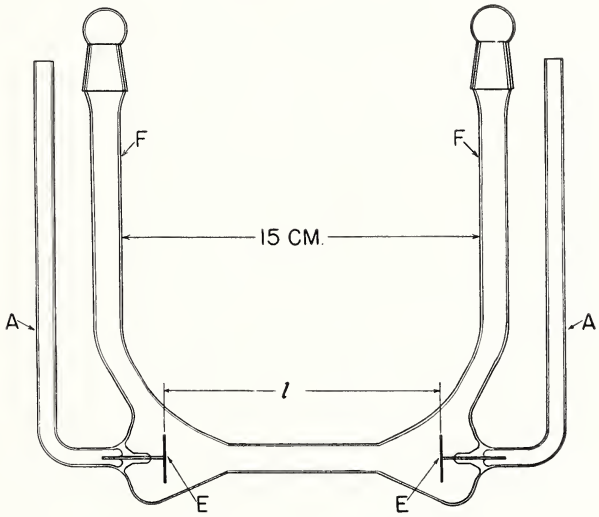

FIGURE 50.—*Precision-type conductivity cell.*

F, Filling tubes; *A*, lead tubes; *E*, electrodes.

The cell must be so designed that the cell constant will remain unchanged under all conditions of the experiment [12, 18]. Unless the cell has been properly constructed, however, its constant changes with the specific resistance and dimensions of the solution being measured and with the frequency of the alternating current [19]. This change in *cell constant* with frequency (this should not be confused with the electrode polarization effect), sometimes called the Parker effect [20], results from the reactive shunts between parts of the cell of opposite polarity in close proximity, such as the filling tubes and lead tubes. This last factor can be made negligible by separating these parts by about 15 cm [18], figure 50. Errors due to the Parker effect may be expected when the "dipping type" cells, figure 51, are used. Since the error in measurement resulting from this Parker effect increases with frequency, and since the electrode polarization reactance decreases with frequency, it is recommended that both be checked by a method described below.

(e) ELECTRODES

Electrodes are usually made of platinum-iridium. They are sometimes platinized to decrease the errors caused by the electrode

polarization. Platinum black has the disadvantage that it is a good catalyzer and may change the conductivity of the solution by increasing the rate of oxidation of sugar therein [21]; therefore, if used, measurements should be made as soon after filling the cell as possible. Palladium black has less catalytic action and is considered more effective, especially at high concentrations [22].

Electrodes are platinized, in the completed cell, by filling it with 0.025 *N* hydrochloric acid solution containing 0.3 percent of platinum chloride and 0.025 percent of lead acetate. A direct current of 0.010 ampere from a battery is passed through the cell, with reversal of polarity every 10 seconds, until the amount of platinum deposited is sufficient [23]. The platinum salt absorbed in the electrodes should be removed by immersing the cell for some hours in warm distilled water which is frequently changed. Removal of the last traces of platinizing liquid and occluded chlorine may be effected by placing the electrodes in a solution of sodium acetate or dilute sulfuric acid and passing a direct current through the electrolyte for about 15 minutes, with reversal of direction every minute.

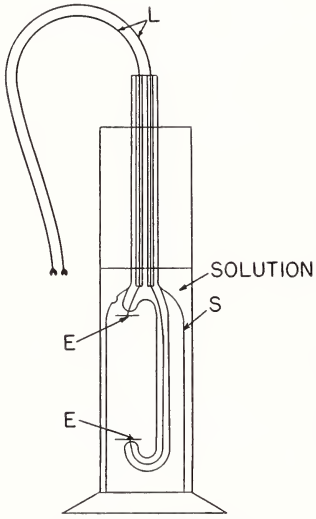

FIGURE 51.—*Dipping-type conductivity cell.*

L, Leads; *E*, electrodes; *S*, electrode cell immersed in solution contained in jar.

Platinized electrodes which have dried are wetted with difficulty, subsequently introducing errors into the measurements by the layer of air bubbles on the surface. To prevent this they should be allowed to rest in distilled water when not in use [24].

The cell constant may change slightly with use, because of changes in the position and surface character of the electrodes, and should be checked regularly with a standard solution of potassium chloride. Should it become necessary to replatinize the electrodes, they may first be deplatinized by electrolyzing aqua regia in the cells for a few minutes reversing the current every minute. Palladium black may be removed in the same manner except that hydrochloric acid is used in place of aqua regia.

(f) CONSTANT-TEMPERATURE BATH

Most solutions encountered in the measurement of conductivity have a high temperature coefficient of about 2 percent per degree centigrade. The desired precision determines the limits within which the temperature must be controlled. Thus with a precision of 0.02 percent, a temperature control to better than 0.01° is required. For this precision the cell should be immersed in a well-stirred bath with adequate regulation, and the bridge current should not produce an appreciable heating effect.

The use of oil in the bath is preferred to water. Oil decreases the errors caused by (1) capacitance bypaths between parts of the cell, (2) capacitance between the cell and the walls of the bath, and (3) electrical eddy currents in the liquid outside the cell. These errors may amount to 0.5 percent or more [11,12].

3. PROCEDURE

(a) EQUILIBRIUM WATER

All solutions on which conductivity determinations are to be made should be prepared from water of low specific conductance. It is possible to obtain water which has a specific conductance of 0.043×10^{-6} mho cm^{-1} at 18° [25]. However, the instant water comes in contact with the air, CO_2 is absorbed and the conductivity increases. When it is brought into equilibrium with the CO_2 in the air, preferably by rapid aeration [26], and has no other impurities, it has a specific conductance of about 0.85×10^{-6} [27]. It also has the pH value 5.7, which can be readily checked with isohydric indicators [26]. (A diaphragm pump of suitable construction is very convenient for spraying outdoor air through a porous Alundum or fritted Pyrex aspirator immersed in the water. Laboratory compressed air generally carries along a spray of oil and impure water.) Such water is known as "equilibrium water." Water having a specific conductance greater than 3×10^{-6} mho cm^{-1} at 25° C may produce a precipitate in the sugar solution, which would alter its conductivity. However, it is possible to secure water of this or lower conductivity from an ordinary laboratory still. If such water is not available, equilibrium water may be prepared directly from tap water [27], but preferably from distilled water, by distillation in a Jena- or Pyrex-glass vessel to which a few milliliters of Nessler solution or alkaline permanganate [28] has been added, and condensing the vapors in a block tin condenser. This water is then thoroughly aerated (overnight generally sufficing) and should be stored in thoroughly steamed and seasoned Pyrex glass-stoppered bottles. It is quite stable over a period of several weeks.

(b) PREPARATION OF POTASSIUM CHLORIDE SOLUTION

The potassium chloride should be selected from the purest material available, recrystallized from conductivity or equilibrium water, separated by centrifugal drainage, fused in a platinum crucible, poured into a platinum dish, and transferred to a closed bottle while still hot. Solutions made from it should be carefully prepared according to the following procedure:

An approximate cell constant is estimated from a rough measurement of the dimensions of the cell. From this value the concentration of potassium chloride is selected from the recommended value in table 33. The correct amount of potassium chloride is weighed into a Pyrex vessel and equilibrium water is added to bring the weight to 1,000 $\pm$0.02 g. The correction to be applied to convert both the weight of the potassium chloride and the solution to weight in vacuum is determined according to directions found in table 114, page 632

TABLE 33.—*Specific conductance (at 1,000 cycles) of potassium chloride solutions, in reciprocal ohm-centimeter*

Solution number	Recommended [1] cell constant		Grams of KCl per 1,000 g of solution in vacuum, C	Specific conductance, K=ohm^{-1} cm^{-1} at—				d 18°/4°
	min	max		0° C	18° C	20° C	25° C	
1	100	5,000	71.3828	0.06543_0	0.09820_1	0.10202_4	0.11173_3	1.04492
2	12	600	7.43344	$.007154_3$	$.011191_9$	$.0116667_8$	$.012886_2$	1.00343
3	1.3	65	0.746558	$.0007751_2$	$.0012226_9$	$.0012757_2$	$.0014114_5$	0.99911
4	0.13	6.5	.074748	----------	.00012740	----------	.00014699	.99867

[1] When the corresponding standard solutions are used in cells that have a cell constant lying between the limits given in this column, the measured resistance will be between 1,000 and 50,000 ohms.

The specific conductances of solutions 1, 2, and 3 in table 33 were determined by Jones and Prendergast [29]. The value for solution 4 was calculated from the empirical equations of Davies [30], which are as follows:

$$\Lambda=149.92-93.85\sqrt{C}+50C \text{ at } 25° \text{ C} \tag{64}$$

$$\Lambda=129.67-79.55\sqrt{C}+35C \text{ at } 18° \text{ C}, \tag{65}$$

where Λ is the equivalent conductance, and C the concentration of the solution in moles per liter. Values calculated from these equations are in agreement with those experimentally determined by Shedlovsky [31], Davies [30], and Johnson and Hulett [32], at 25° C., and with those of Shedlovsky [33], as well as Davies [30], at 18° C. The specific conductance is determined from the equivalent conductance by equation

$$k=\Lambda\eta, \tag{66}$$

where k is the specific conductance, and η the concentration in equivalents per milliliter (not per liter).

In order to calculate the concentration of solution 4 in grams of potassium chloride per 1,000 g of solution, the density of a 0.001 N KCl solution at 25° C was determined by methods of interpolation from data found in the International Critical Tables. This density is based on a solution which contains 0.074533 g of KCl per liter at 25° C.

(c) DETERMINATION OF CELL CONSTANTS

The resistance, $R_{\text{solv.}}$, of equilibrium water from the same lot as that used in making the potassium chloride solutions is checked in a clean cell [12, 34]. The cell is rinsed two or three times with the potassium chloride solution and then filled therewith. It is allowed to remain 15 or 20 minutes in the constant-temperature bath. The resistance of the solution is then determined, and redetermined at the end of 5 minutes. If the two resistances check, the solution has reached thermal equilibrium. To verify the cleanliness of the cell, a second determination should be made after rinsing and filling it with fresh solution. The final value of the resistance, $R_{\text{soln.}}$, is used to determine the cell constant (uncorrected for solvent conductivity) by means of the equation

$$\left(\frac{l}{a}\right) \text{uncorrected} =k\frac{C_1}{C}R_{\text{soln.}}, \tag{67}$$

in which k is the specific conductance of a standard potassium chloride solution (from table 33); C, the concentration in grams of potassium chloride per 1,000 g of solution corresponding to this specific conductance; and C_1, the actual concentration of the solution. Both C and C_1 are expressed in grams of potassium chloride per 1,000 g of solution, corrected to weight in vacuum. Since the change in specific conductance of a potassium chloride solution with concentration is not constant, the value of C_1 should be made as nearly equal to C as possible.

The uncorrected value of the cell constant, as determined from eq 67, may be used to determine the approximate specific conductance, $K_{\text{solv.}}$, of the equilibrium water by means of the equation

$$K_{\text{solv.}}=\left(\frac{l}{a}\right)\text{uncorrected}\times\frac{1}{R_{\text{solv.}}}. \tag{68}$$

Since the specific conductance of the solution, $K_{\text{soln.}}$, is the sum of the specific conductance of the potassium chloride ions, K_{KCl}, plus the specific conductance of the ions present in the equilibrium water, $K_{\text{solv.}}$, a very close approximation of the cell constant may be calculated from the equation

$$\frac{l}{a}=\left(K\frac{C_1}{C}+K_{\text{solv.}}\right)R_{\text{soln.}}. \tag{68a}$$

A more accurate method would be to make two resistance measurements, R' and R'', extrapolated for infinite frequency, on two standard solutions of known specific conductance, K' and K''. Then

$$\frac{l}{a}=(K'-K'')\left(\frac{1}{R'}-\frac{1}{R''}\right). \tag{68b}$$

All measurements should be made at the temperature and frequency corresponding to that at which the conductance values of the standard potassium chloride solution were determined.

The cell constant, $(l/a)_t$, at any temperature, t, may be computed from the cell constant, $(l/a)_0$, at 0°, according to the following equation [35]:

$$\left(\frac{l}{a}\right)_t=\left(\frac{l}{a}\right)_0(1-\alpha t), \tag{69}$$

where α is the linear coefficient of expansion of the glass from which the cell is constructed. For Jena normal 16 III glass, $\alpha=8.08\times10^{-6}$ [36], and for Pyrex glass, $\alpha=3.6\times10^{-6}$ [37].

Cells should be selected which have constants of such values that the total measured resistance of solutions of the electrolytes will lie between the limits of 1,000 and 50,000 ohms [35]. The highest resistance of any of the solutions measured will be that of equilibrium water, which should have a specific conductance not greater than 3.0×10^{-6} and the lowest resistance, that of molasses, which may have a specific conductance as high as 5×10^{-2}. Three cell constants will cover this range and yet fall within the limits of resistance given above. These are 0.15, 7.5, and 50.0 reciprocal centimeters. If the specific conductance covers a narrow range, a single cell may suffice.

(d) CHECKING OF CELLS

The best test for the quality of the cells, whether they have bright or platinized electrodes, and for sufficiency of platinization, is to note the change in resistance resulting from a change in frequency of the oscillator current [38].

If electrode polarization reactance be treated as a function of the frequency, it follows that this reactance may be determined by successively measuring the resistance of the solution at two frequencies,

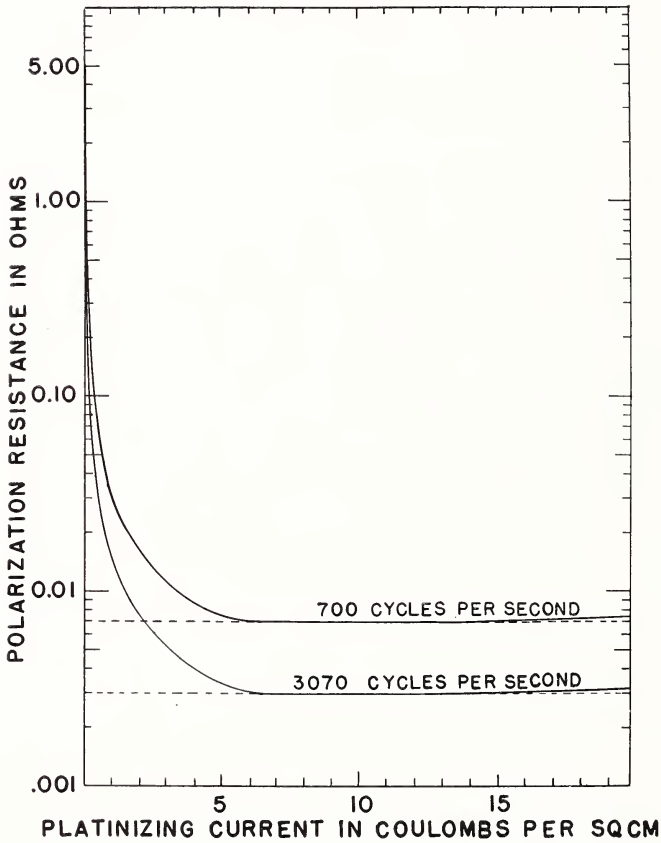

FIGURE 52.—*Polarization reactance versus platinization.*

one of which is about four times as great as the other. Whenever the difference between these two measurements is negligible for the purpose of the measurement, then the deposit of platinum black is adequate. (Fig. 52 [17] shows how the platinization of electrodes reduces this reactance.) However, if the two measurements indicate that a correction should be made, the true resistance may be found by extrapolating the data to infinite frequency [12, 15]. This may be done graphically or in the following manner:

Let R_1 and R_2 be the resistance measurements at two frequencies, f_1 and f_2, respectively. Then, if the electrode polarization reactance,

ΔR, is inversely proportional to some function, n, of the frequency

or

$$\left.\begin{aligned}\Delta R&=k/f^n\\ k&=\Delta R f^n\end{aligned}\right\}, \tag{70}$$

where k is the proportionality factor. The true resistance, R_T, of the solution is equal to the measured resistance minus the electrode polarization reactance or

$$R_T=R_1-\Delta R_1=R_2-\Delta R_2$$

or

$$R_T=R_1-k/f_1^n=R_2-k/f_2^n,$$

from which

$$k=\frac{R_1-R_2}{\frac{1}{f_1^n}-\frac{1}{f_2^n}} \tag{71}$$

and

$$R_T=R_1-\frac{R_1-R_2}{1-\left(\frac{f_1}{f_2}\right)^n}. \tag{72}$$

Early observers have used unity for the value of n [15], but in a recent investigation 1/2 has been used [17]. It must be remembered that the use of the above equations is valid only when other errors in measurement resulting from changes in frequency (such as from the Parker effect) have been eliminated.

When routine measurements, such as those encountered in factory operations, are being made, no correction for electrode polarization reactance need be estimated. The frequency used for the observation should be recorded if it is to be compared with other data.

4. SPECIFIC CONDUCTANCE OF SOLUTIONS OF SUGAR PRODUCTS

(a) ASH DETERMINATION BY THE "*C*-RATIO" METHOD

"*C*-ratio" is defined as the ratio of the percentage of ash determined by incineration, as in chapter XVI, p. 263, to the specific conductance. After this factor has been established by averaging the results of several determinations of gravimetric ash and specific conductance, it may then be used to determine the percentage of ash of similar products by substituting its value and measured values of specific conductance in the equation

$$\text{Percentage of ash}=C\text{-ratio}\times\text{specific conductance}. \tag{73}$$

This method of determining ash is applicable to control work of individual sugar manufacturers and to the ash analysis of granulated and other refined sugars [39]. However, since the specific-conductance value alone may be used to predict the performance of the product, many prefer to use it without conversion to percentage ash for control work.

Specific-conductance determinations are made in cells of predetermined cell constant at a temperature most convenient for the locality, by measuring, as described above, the resistance of a solution of the product in equilibrium water and substituting this value in eq 63. The value of the specific conductance of the equilibrium water should be subtracted from the value found for the solution before the calculation of the C-ratio is made.

If the solutions are heated or subjected to vacuum, the value of K_{solv} will be changed from loss of CO_2; if high precision is required, the value of K_{solv} should be redetermined on a sample of the equilibrium water treated in the same manner as the solution.

The concentration of the solution recommended by different observers varies from 2.5 g of dry substance per 100 ml to 50 g per 100 ml. Since the conductivity of solutions of beet-sugar products passes through a maximum at 25 g of sucrose per 100 ml of solution [8], measurements made near this concentration will be affected less by slight errors in concentration than at other concentrations [40]. Regardless of what concentration is selected as being the most suitable, it should be the same as that used for the determination of the C-ratio.

(b) ZERBAN AND SATTLER CONDUCTANCE METHOD FOR ASH

Although the C-ratio method may be used to determine the ash content of sugars from the same source in any one season, the ratio determined for one district cannot be used for another district. This fact has resulted in the Zerban and Sattler method for ash determination, based on conductivity measurements under special conditions, and no reference need be made to the gravimetric ash.

In developing this method, they minimize all causes for variability of the C-ratio except that resulting from the composition of the dissolved salts. The inorganic salts in solution in raw sugars are principally sulfates and chlorides. Since the equivalent conductance of solutions containing anions of inorganic salts is considerably higher than that of solutions containing anions of organic salts derived from the same base, it follows that the specific conductance of a solution containing a large percentage of chlorides or sulfates in the ash is relatively greater than that of a solution containing a small percentage. Furthermore, the C-ratio will decrease as the percentage of inorganic anions in the ash increases.

If hydrochloric acid is added to a solution containing only inorganic anions, the specific conductance will increase linearly with the addition of acid. However, if the solution contains both organic and inorganic anions, the specific conductance will increase linearly only after the weaker inorganic anions have been displaced by those of the added acid.

A similar relationship exists between the specific conductance of solutions containing inorganic and organic cations if a solution of potassium hydroxide is added. However, except when the sugar product has received treatment with bone black, this latter relationship is not pronounced and may be ignored.

From these relationships, Zerban and Sattler have developed three general methods for the determination of ash applicable to:

1. Raw cane and soft sugars [41].

2. Refinery sirups and molasses produced without char treatment [42].
3. Raw and refinery sirups and molasses of unknown origin [43].

(1) Raw Cane and Soft Sugars [40].—Twenty-five grams of sugar is dissolved in equilibrium water and the solution diluted to 500 ml at 20° C. The specific conductance, k, of one portion of this solution is determined and likewise, the specific conductance, k_1, of another portion to which 5 ml of 0.25 N hydrochloric acid has been added to each 200 ml. Corrections are made for temperature and the conductivity of the water. The corrected specific conductances multiplied by 10^6 give, respectively, K for the original solution, and K_1 for the acidified solution. The percentage of ash may then be computed from the empirical equations,

$$\text{Raw sugar, percentage of ash} = 0.001757 \times (0.913K + 193.5 - 0.1K_1) \tag{74}$$

$$\text{Soft sugar, percentage of ash} = 0.001695 \times (0.913K + 193.5 - 0.1K_1) \tag{75}$$

The temperature corrections for k and k_1 are given by the equations

$$(k) = (k)_{20}\,[1 + 0.02234(t-20) + 0.0000885(t-20)^2] \tag{76}$$

$$(k_1)_t = (k_1)_{20}[1 + 0.01704(t-20) + 0.000062(t-20)^2], \tag{77}$$

in which t is the temperature at which the conductivity determination is made. The correction for $(k)_t$ is roughly 2.2 percent per degree centigrade if measurements are made near 20° C.

The concentration of the acid may be checked by conductivity determinations. When 5 ml of the 0.25 N acid is mixed with 200 ml of equilibrium water the corrected specific conductance is 0.002370 at 20° C.

(2) Refinery Sirups and Molasses Produced Without Char Treatment [41].—A solution is made of 100 ml of hot equilibrium water and 25 g of sirup or molasses. It is filtered with vacuum through asbestos and filter-paper pulp into a 200-ml volumetric flask with repeated washing with hot equilibrium water. The filtrate is mixed thoroughly and diluted with equilibrium water to 200 ml at 20° C. To a 20-ml portion of the filtrate is added 22.5 g of pure tablet sugar. This is diluted to 500 ml at 20° C with equilibrium water. This is known as solution A. To 200 ml of solution A, 5 ml of 0.25 N hydrochloric acid is added. This is known as solution B.

The specific conductances are determined in both solutions A and B and are corrected for solvent, specific conductance of the tablet sugar, and temperature. These values multiplied by 10^6 are respectively K and K_1, which may be substituted in the equation

$$\text{Percentage of ash} = 0.001757(9.13K + 1935 - K_1). \tag{78}$$

(3) Raw and Refinery Sirups and Molasses of Unknown Origin [42].—The procedure is the same as that used for the preceding determinations except that three conductivity measurements are required. Normal orthophosphoric acid is added to solution A to obtain solution B. The specific conductance at 20° C is determined on each of the following solutions:

1. k of solution A, as prepared in the preceding section.

2. k_1 of solution A, to which has been added 5 ml of 0.025 N potassium hydroxide per 200 ml.

3. k_2 of solution A, to which has been added 5 ml of normal orthophosphoric acid per 200 ml.

Each of the three specific conductances so determined are corrected for the specific conductance of the equilibrium water used and for the specific conductance of the tablet sugar. The corrected values multiplied by 10^6 are respectively K, K_2, and K_3. The percentage of ash is then determined by substituting these values in the equation

$$\text{Percentage of ash} = 0.0191369K - 0.002249K_2 - 0.001210\,K_3 + 3.07. \tag{79}$$

The concentration of the acid may be checked by conductivity determinations. When 5 ml of the normal orthophosphoric acid is added to 200 ml of equilibrium water the corrected specific conductance is 1925×10^{-6} at 20° C.

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XVIII. MEASUREMENT OF HYDROGEN-ION CONCENTRATION

1. INTRODUCTION

Bates and Associates [1] in 1920 reported results giving the hydrogen-ion concentration of aqueous solutions of a number of commercial sugars. In 1922 Brewster and Raines [2] published an account of the use of hydrogen-ion methods for reaction-control in cane juices in the experimental manufacture of sugar. Balch and Paine [28] in 1925 described a scheme for the automatic recording of hydrogen-ion concentration in lime-treated cane juice. These appear to be the earliest recorded instances of the application of such methods (now regarded as indispensable) to commercial sugar products and their manufacture. These were followed shortly by the development of apparatus for the automatic dosage of cane or beet juices with lime or carbon dioxide to a desired end point controlled by electrodes reacting to the pH of the liquid, the resulting pH being simultaneously recorded.

Prior to the advent of hydrogen-ion methods, the adjustment of reaction in sugar juices was based upon the titration of a quantity with standard acid or alkali to an indicator end point. This gave a measure of the quantity of acid or alkali present. Hydrogen-ion methods, on the other hand, give information regarding the intensity of reaction of acid or alkali due to the concentration of hydrogen (or hydroxyl) ions, which influence the rate of inversion of sucrose, and the clarification, filtration, and decolorization of juices, as is well known.

The nomenclature of hydrogen-ion concentration is based upon the normal weight (1.008 g) of ionized hydrogen in a liter of solution. This may be expressed fractionally as 1/1 N. A solution containing 0.01008 g of hydrogen ions per liter would be 1/100 N, and so on. If these fractions are expressed as powers of 10, we have $1/1=10^0$, $1/10=10^{-1}$, $1/100=10^{-2}$, . . . $1/1{,}000{,}000=10^{-6}$, and so on. The negative exponent, which may or may not be a whole number, is the logarithm of the reciprocal of the hydrogen-ion concentration, log $1/[H^+]$ (the brackets indicate normality). To this has been assigned the symbol pH. The numerical value of pH is sometimes called the hydrogen-ion exponent. Instead of using fractions, we therefore write pH=1, pH=6, pH=8.4, etc. Also one may say that the pH value of a solution is the logarithm of the number of liters that contain 1 gram-ion of hydrogen. Thus in pure water, at the ordinary temperature, it requires 10 million liters to yield 1.008 g of ionized hydrogen. The log of 10,000,000 is 7. Therefore the pH of pure water is 7.

In all neutral aqueous solutions, as well as in pure water, pH+pOH=14 at the ordinary temperature, and the products of dissociation, H^+ and OH^- ions, are present in equal amounts, so that pH=pOH=7. The expression, pOH, which might be taken for the purpose of expressing alkalinity, ordinarily is not used, since, as may be seen by reference to the two equations, values of pH below 7 indicate an excess of H^+ over OH^- ions, and the solution is said to be acid. Similarly, when pH values are above 7, the OH^- ions are in excess and the solution is said to be alkaline.

The so-called strength of a pure acid or alkali in solution depends upon the degree of ionization and the hydrogen-ion concentration of such solutions may be calculated from the ionization constant. If a strong acid or alkali be added little by little to water, the hydrogen-ion concentration changes enormously with each addition. If, however, a soluble salt of the acid or base be present, the ionization is depressed and upon the addition of the one or the other the change in hydrogen-ion concentration is gradual and may be controlled within certain limits. This resistance to change in pH due to the presence of a salt is called buffer action. Buffer action also results from the presence of salts of bases with weak acids as encountered in most plant juices and accounts for the very gradual increase in hydrogen-ion concentration of cane juice when the latter is treated with sulfur dioxide. Advantage is taken of the buffer action of certain salts in the preparation of standard solutions for colorimetric pH methods, as described later.

Methods for the measurement of hydrogen-ion concentration may be divided into two categories (a) potentiometric methods, whereby is measured, under proper conditions, the potential of a concentration cell, of which the unknown solution is a part, and (b) colorimetric methods depending upon the use of indicators, the color or shade of color of which changes with variation in hydrogen-ion concentration. It is advantageous to have both potentiometric and colorimetric methods available.

2. POTENTIOMETRIC METHODS

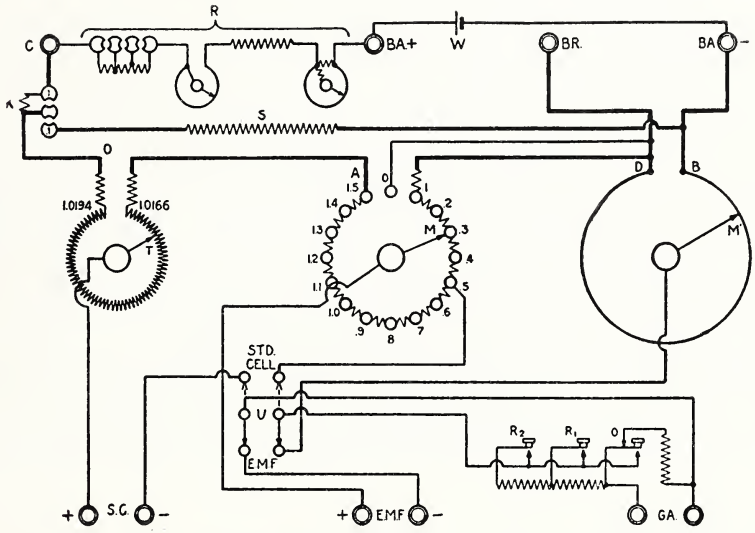
(a) POTENTIOMETERS

The electromotive force (emf) of a concentration cell is measured by balancing against it a measurable potential from an external source. At balance no current passes through the cell, as indicated by the null-point instrument. The apparatus employed consists of a potentiometer; a galvanometer as indicating instrument; an outside source of emf, such as that furnished by dry cells or a storage cell, the value of which is known by reference to a standard cell, the last-named being usually a Weston cadmium-mercury cell.

Potentiometers are available in several forms, some of which are highly accurate and used in research and for calibrating other instruments. Others intended for industrial laboratory and plant use, although having sufficient accuracy, are portable, with galvanometer, standard cell, and measuring device in a single housing, or with all accessories, including glass and reference electrodes, amplifying tubes, and voltage supply housed within a small space. The choice of apparatus is dictated by the accuracy required and by the nature of the material in which measurements are to be made.

A diagram of the Leeds & Northrup type *K* potentiometer is shown in figure 53, which, with the description that follows, illustrates the potentiometric principle and the operation of the instrument. In figure 54 the instrument is shown in use with a hydrogen gas-calomel cell. The standard cell, galvanometer, and dry cells also are shown.

In the diagram the portions of the bridge by which measurements are made consist of fifteen 5-ohm coils in series in the circuit *AD* (contact made with *M*), and in series with them the extended wire *DB*, the resistance of which is also 5 ohms. The scale of *DB*, shown in the photograph, reads from 0 to 1,100. Contact with the extended wire is made by the moving contact, *M'*. Current from the battery, *W*, flows through these resistances and may be made exactly 0.02 ampere by means of the regulating rheostat, *R*. This is done by setting the double-throw switch to "std. cell", which connects the standard cell in series with the galvanometer, G, and the tapping keys,



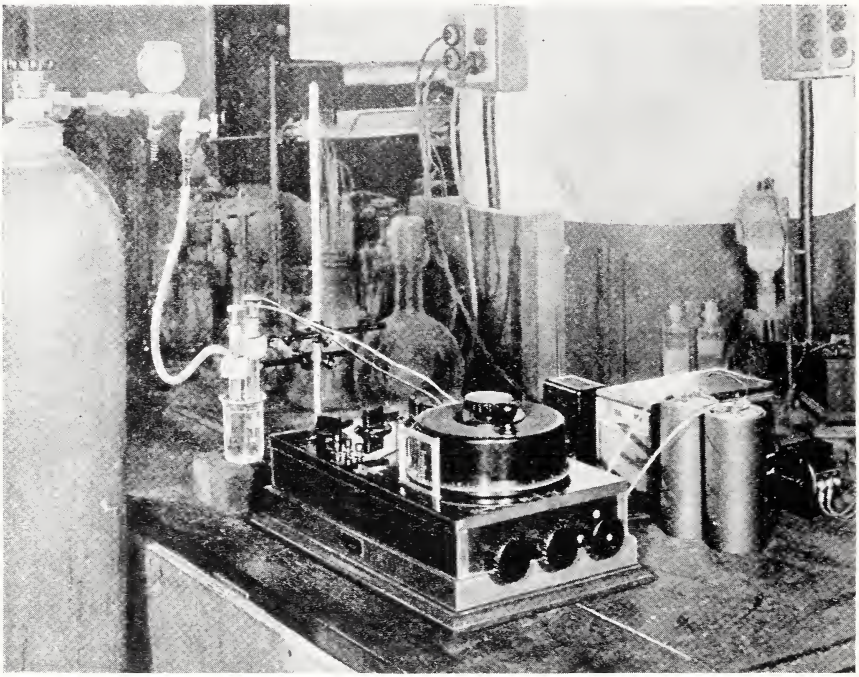
Courtesy of Leeds & Northrup Co.

FIGURE 53.—*Wiring diagram of type K potentiometer*

R_1, R_2, and R_3, and with the point .5 on *AD*, to which one point on the double-throw switch is wired. Between *A* and *O* there is a series of resistances with a sliding contact, *T*. The resistance between the points .5 and *A* is exactly that which corresponds with the emf of 1 volt, and between 1.0166 and .5 a sufficient resistance is added to make the resistance between these points correspond exactly with an emf of 1.0166 volts. The small circular slide wire connected at 1.0166 makes contact with the standard cell through the contact, *T*. The resistance value of this slide wire is such that a practically continuous variation can be obtained in the standard-cell circuit voltages from 1.0166 to 1.0194, a range corresponding with the variations in different standard cadmium cells. To adjust the current to 0.02 ampere, with the switch thrown to the "std. cell" position, the contact, *T*, is set to correspond with the standard cell voltage and rheostat, *R*, is regulated until the galvanometer shows no deflection. The unknown emf is

now measured by throwing the switch to the emf position and adjusting the resistances with M and M' by touching the contact keys, R_2, R_1, and R, until there is again no galvanometer deflection. After this measurement is made the working current may again be checked against the standard cell, as described.

In figure 55 is shown a Leeds & Northrup potentiometer-electrometer with range from 0 to 1.100 volts. This portable instrument contains a stage of amplification and is suitable for pH measurements



Courtesy of Leeds & Northrup Co.

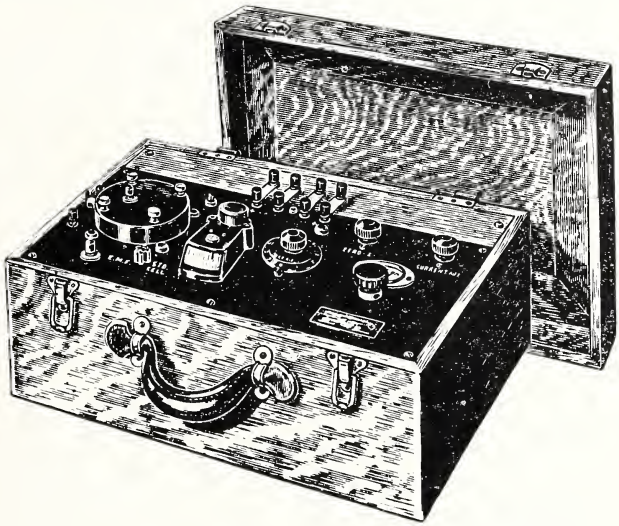
FIGURE 54.—*Leeds & Northrup type K potentiometer with hydrogen-gas electrode, calomel electrode, etc.*

with all types of electrodes, including glass. Other types of potentiometers are illustrated in figure 59, A and B.

(b) CALOMEL ELECTRODES

Various forms of calomel electrode vessels are shown in figure 56. The bulb at the bottom of the cell (C, D, E) is filled with a layer of pure mercury. On this rests a layer of pure calomel mixed with mercury, and the filling of the cell is completed with a solution of potassium chloride having a definite concentration and saturated with calomel. One of three concentrations of potassium chloride is customarily used, either 0.1 M, 1.0 M, or saturated, and in reference to these concentrations the terms "tenth-normal", "normal", or "saturated" calomel electrodes are used as abbreviations. By means of side-tubes the cells communicate with a reservoir of saturated potassium chloride which by turning the stopcock at the top of the cell may be allowed to fill the side arm and form the necessary salt bridge between the calomel

electrode and the unknown solution. Electrical connection between the electrode and the potentiometer is made through platinum wire sealed into the bottom of the vessel and either wired directly, as in *D*, or through a short column of mercury in the small glass tubes sealed at the bottom of the electrode (*C* and *D*). In the dipping electrodes,



Courtesy of Leeds & Northrup Co.

FIGURE 55.—*Potentiometer-electrometer.*

A and *B*, the calomel electrode proper is contained in the small inner tube, which, near the bottom and just above the calomel layer, has a small opening through which the electrode communicates with the potassium chloride solution contained in the outer jacket. This

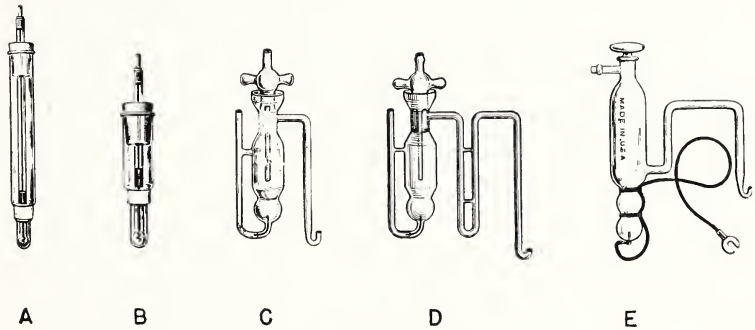


FIGURE 56.—*Types of calomel electrodes.*

jacket is closed by a ground joint which is moistened with potassium chloride solution which passes the current when immersed in the test solution.

It is essential that pure materials be used in preparing the electrodes in order that they may have the accepted emf values. Mercury may be purified by allowing it to fall in a fine spray through diluted nitric

acid. It is then washed with distilled water, dried, and distilled in vacuo. Reilly and Rae [4] give the following directions for purifying mercury by electrolysis: "The mercury is placed in a large dish inside which is a small dish containing a small quantity of mercury. Platinum-wire electrodes sealed into glass tubes make contact with the two portions of mercury, that in the smaller vessel being the cathode. An electrolyte, consisting of 90 parts of water, 5 parts of sulfuric acid, and 5 parts of nitric acid, is poured in so as to cover the upper edge of the smaller vessel to a depth of 2 cm. A current of 0.5 ampere is passed for 2 hours for each kilogram of mercury in the outer vessel. The mercury in the outer vessel is then removed, washed, dried, and distilled in vacuo."

For the preparation of calomel a portion of the purified mercury is dissolved in pure nitric acid that has been redistilled and slightly diluted. The mercury nitrate solution is poured into a large excess of distilled water containing some nitric acid. To this solution is slowly added dilute hydrochloric acid purified by distilling pure 20-percent acid, discarding the first and last portions of the distillate. The precipitate is repeatedly washed with distilled water, preferably by decantation. Some free mercury should be present throughout the process to prevent the formation of mercuric salt. At the completion of washing, the calomel should be intimately mixed with finely divided mercury by shaking.

TABLE 34.—*Arbitrarily standardized values for half-cells* [1]

Half-cell I	$\|(H^+)=1\|H_2$ (1 atm), Pt.
Half-cell II	KCl (sat.)|KCl (0.1 *N*), HgCl|Hg.
Half-cell III	KCl (sat.), HgCl|Hg.
Half-cell IV	KCl (sat.)|HCl (0.1 *N*)|H_2 (1 atm), Pt.
Half-cell V	KCl (sat.)|KH phthalate (0.05 *M*)|H_2 (1 atm), Pt.
Half-cell VI	KCl (sat.)|Acetic acid (0.1 *N*), Na acetate (0.1 *M*)|H_2(1 atm), Pt.
Half-cell VII	$\|(H^+)=1$, quinhydrone|Pt.
Half-cell VIII	KCl (sat.)|HCl (0.1 *N*), quinhydrone|Pt.

Temperature	Half-cell							
	I	II	III	IV	V	VI	VII	VIII
°C	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*	*Volts*
18	0.0000	0.3380	0.251	−0.0621	(−0.229)	−0.2668	0.7044	0.6423
20	.0000	.3379	.250	−.0625	−.2310	−.2686	.7029	.6404
25	.0000	.3376	.2458	−.0636	(−.235)	−.2732	.6992	.6356
30	.0000	.3371	.242	−.0647	(−.239)	----------	.6955	.6308
35	.0000	.3365	.238	−.0657	----------	----------	.6918	.6261
38	.0000	.3361	.236	−.0664	----------	----------	.6896	.6232
40	.0000	.3358	.234	−.0668	----------	----------	.6881	.6213

[1] W. M. Clark, The Determination of Hydrogen Ions, 3d. ed., p. 672 (Williams & Wilkins Co., Baltimore, Md., 1928).

The calomel-mercury mixture, before being placed in the vessel, is repeatedly shaken with small quantities of the potassium chloride solution chosen for the cell. The potassium chloride solution used to complete the filling of the cell is also saturated with calomel. The calomel half-cell may be connected directly with the test solution or through a salt bridge formed usually by a saturated solution of potassium chloride flowing from a reservoir through a side arm of the vessel and making contact with the calomel-saturated potassium chloride of the cell. After a measurement, the solution at the end of the side arm may be flushed out by slightly turning the stopcock.

In electrodes A and B (fig. 56) the larger outside tube contains saturated potassium chloride and the inner tube is the calomel electrode proper.

Clark's [3] table of values for several half-cells commonly used in the determination of hydrogen-ion concentration is reproduced in table 34. It is pointed out by Clark that discrepancies may be found in certain values given in the table and that certain values are to be regarded as tentative. This applies particularly to the temperature error in the saturated calomel half-cell. "On the other hand, the potential of a cell composed of a hydrogen or quinhydrone half-cell and a saturated potassium chloride calomel half-cell has a small temperature coefficient . . . so that the temperature value may be in considerable error without causing great error in potential."

(c) HYDROGEN ELECTRODES

A hydrogen electrode is formed by saturating platinum black (coated on platinum foil or wire for rigidity) with hydrogen gas. When such an electrode is placed in contact with a solution containing hydrogen ions, a difference of potential is established at the electrode-solution interface analogous to the potential difference between a metal electrode and a solution containing its ions. The emf of such a half-cell is not directly measurable, but if two half-cells be connected so that the electrolytes form a sharp liquid junction, the total emf of the concentration cell so formed may be measured potentiometrically. If the emf of one half-cell is known, that of the other may be computed.

The emf of such a concentration cell, ignoring the liquid-junction potential, is represented by

$$E=\frac{RT}{nF}\ln\frac{C}{C_1}, \tag{80}$$

where R is the gas constant=8.31507 volt-coulombs in absolute units; T is the absolute temperature=$273.1+t°$ C; n is the valency of the electrode element; and F (the faraday) is the charge on 1 g equivalent of the ion=96,500 coulombs. C and C_1 are the ion concentrations in the two halves of the cell. Substituting and multiplying by 2.3026 to convert to common logarithms, we obtain

$$E=0.000198406\frac{T}{n}\log\frac{C}{C_1}. \tag{81}$$

Since measurements of E are customarily made in terms of international volts instead of absolute units, the numerical value in eq 81 is converted by dividing by 1.00042 [3, p. 250], and we obtain

$$E=0.000198322\frac{T}{n}\log\frac{C}{C_1}. \tag{82}$$

For the hydrogen electrode, let us assume that the concentration in one of the half-cells is normal with respect to hydrogen ions (1.008 g/liter) and write $C=1$, and in the other half-cell let the hydrogen-ion concentration be unknown and write $C_1=[H^+]$. The valence, $n=1$, and eq 82 then becomes

$$E=0.000198322T\log\frac{1}{[H^+]}, \tag{83}$$

and since $\log \frac{1}{[H^+]} = pH$, [12] we have

$$pH = \frac{E}{0.000198322T} \tag{84}$$

or at 25° C

$$pH = \frac{E}{0.05912}. \tag{85}$$

The normal hydrogen half-cell is not used as a reference standard in practical pH measurements. As a primary standard of reference, Clark [3, p. 480] recommends the 0. 1 N calomel half-cell, referred to the potential of the normal hydrogen half-cell as equal to zero, and specifies as follows:

"It shall be assumed, arbitrarily, that in the cell Pt, H_2 (1 atmos.) $|\underset{A}{}$ H^+ (activity, x) $|\underset{B}{}$ KCl (sat.) $|\underset{C}{}$ KCl (0.1 N), HgCl(sat.) $|\underset{D}{}$ Hg the potential difference at B remains constant as x varies and that the sum of the potential differences at B, C, and D is as follows at each indicated temperature. [These values are given in table 34, column 2.]

"The standard experimental meaning of pH shall be the potential of the above cell considered as of positive numerical value, less the above value for the calomel half-cell pertaining to the temperature used, the difference being divided by the numerical quantity $0.000198322T$, where T is the absolute temperature."

The statement of the last paragraph may be formulated in the equation

$$pH = \frac{E - E(\text{cal})}{0.000198322T}. \tag{86}$$

This does not preclude the use of secondary standards, such as the saturated calomel half-cell or the quinhydrone electrode, but the "attempt shall be made to use this standard in accordance with the specifications made above."

Hydrogen-electrode potentials vary with barometric pressure, and the apparatus should be so constructed that the gas pressure in the half-cell is the same as that of the surrounding atmosphere. In most routine measurements, a barometric correction may be omitted, but it should be included for exact measurements. The corrected value of pH is obtained by

$$pH = \frac{E + E\ (\text{bar.}) - E\ (\text{cal})}{0.000198322T},$$

and the correction value E (bar.) is found by

$$E\ (\text{bar.}) = \frac{0.000198322T}{2} \log \frac{760}{x},$$

[12] Clark [3, p. 479] states: "Originally pH was defined by $pH = \log \frac{1}{[H^+]}$. Actually the numerical values called pH have been determined by dividing the potential of a hydrogen cell by $2.3026RT/F$. In the comparison of one solution with a standard solution of hydrion activity of unity, the rigid relation may be written

$$\log \frac{1}{(H^+)} = \frac{-EF}{2.3026RT},$$

where (H^+) represents the hydrogen-ion activity of the solution under investigation. Consequently, the measured values called pH are $\log \frac{1}{(H^+)}$."

where x is the value found by subtracting the pressure of aqueous vapor at the temperature, $t°$ C, from the barometer reading.

The hydrogen electrode is used for the standardization of buffer solutions and for checking methods in which other electrodes are used. It is useful in properly buffered solutions over a range of 0.0 to 14.0 pH. It is inaccurate in the presence of certain metals and dissolved gases and in the presence of sulfites or sulfurous acid. The coating of platinum black is sometimes clogged or "poisoned" and rendered inactive.

The Clark rocking-electrode assembly, consisting of hydrogen and calomel electrodes, is shown in detail in figure 57, and mounted for use in figure 58 (E). The hydrogen electrode vessel, shown at E (fig. 57) is mounted in a clamp pivoted behind the rubber connection between J and H. This clamp runs in a groove of the eccentric, I, the

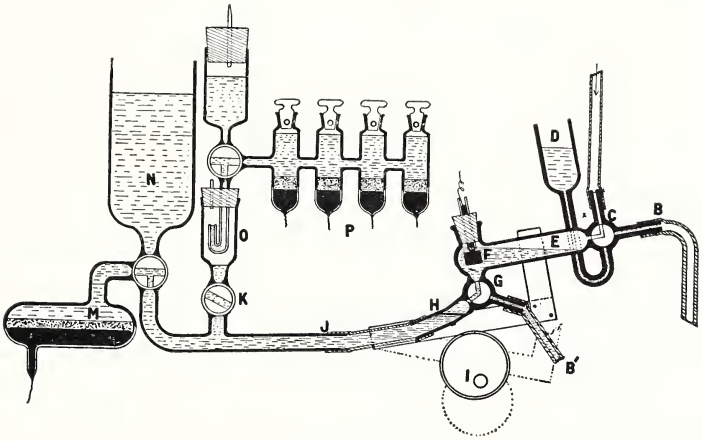


FIGURE 57.—*Clark rocking electrode.*

rotation of which rocks the vessel. With the hydrogen electrode inserted at F, the vessel is filled as full as possible with water from D through cock C. The water is displaced with hydrogen through A after turning C to communicate with drain, B, and the vessel is flushed with succeeding changes of hydrogen. The vessel is rocked back toward C, which is closed, and the test solution is run in from reservoir, D, with G open toward B' until the vessel is half full.

Cock G is now closed and cock C is opened so that hydrogen may enter through A to exert a continuous pressure on the liquid. The solution is then rocked until equilibrium is established with the liquid. The rocking alternately completely immerses and then exposes the electrode to the hydrogen gas.

At M is a saturated potassium chloride–calomel electrode used as a working standard, and at N is a reservoir containing saturated potassium chloride used in making liquid junctions. At P is a battery of accurately made 0.1 N calomel electrodes used in standardizing the saturated calomel working cell. This battery may be connected with the system through the liquid junction at O by opening cock K. To measure the emf, the rocking is stopped, and E is opened so that a small amount of saturated potassium chloride may escape through

B' while the rubber tube between J and H is pinched. Cock E is turned so that E and H communicate and liquid flows into H to form a liquid junction with the saturated potassium chloride salt bridge.

Measurement is made with the potentiometer to give a combined emf for the entire chain which, let us assume, is 0.645v at 25° C. The emf of the saturated calomel half-cell and potassium chloride salt bridge at 25° C. as given by Clark, is 0.2458v. Then

$$\mathrm{pH}=\frac{0.645-0.2458}{0.05912}=6.92,$$

the barometric correction being ignored.

Simpler forms of hydrogen electrodes that are satisfactory are illustrated in figure 58. Electrodes A and C are made of platinum

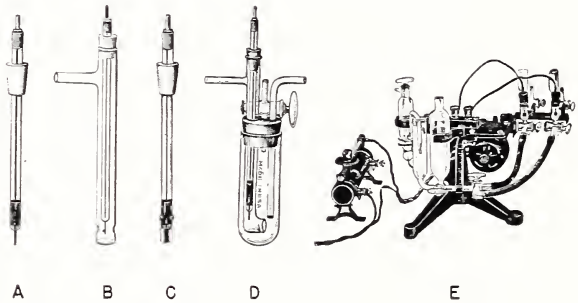


FIGURE 58.—*Various types of hydrogen electrodes.*
A, B, C, D, dipping electrodes; *E,* rocking electrode.
Courtesy of Leeds & Northrup Co.

wire and foil, respectively, sealed into glass tubing, contact with the wire leading to the potentiometer being made through mercury contained in the tubing. At B and D are shown the electrodes in glass jackets which are connected with the supply of hydrogen gas by rubber tubing fitted to the side arm. Hydrogen under slight pressure bubbles from the bottom openings of the jacket, alternately bathing the electrode with hydrogen and with solution. When the solution has become saturated with hydrogen, the flow of gas is stopped and the emf is measured.

For the deposition of platinum or palladium black on bright platinum, Clark electrolyzes a 3-percent solution of the chloride of either metal, acidified with hydrochloric acid. The current from a 4-volt storage battery is allowed to produce a vigorous evolution of gas until the coating of black conceals the glint of the metal. The coated electrode as negative, is then placed in a dilute solution of sulfuric acid and electrolyzed to charge with hydrogen. The bubbles should come off evenly and the electrode should be evenly coated. The deposit should adhere under a vigorous stream of water and the electrodes should not be allowed to become dry. In use, electrodes frequently become clogged, poisoned, or otherwise unfitted for further use. The black should then be removed and the metal recoated. To remove the deposit of black, the electrode is connected to the positive pole of the battery and immersed in 1:1 hydrochloric acid which is electrolyzed. Palladium is more easily removed by electrolysis than

is platinum. The latter, however, is easily removed if the platinum electrode is plated with gold before the black is deposited.

(d) QUINHYDRONE ELECTRODE

The quinhydrone electrode (or half-cell), because of its simplicity and ease of manipulation, has been widely used for pH measurement.

To make a measurement, the platinum or gold electrode is immersed in the test solution and a small amount of quinhydrone, which is sparingly soluble, is added and the potential is measured against a saturated calomel half-cell in liquid junction with the solution.

To calculate the pH of the solution from the observed potential, Biilmann [5], whose investigations contributed largely to our knowledge of the quinhydrone electrode, used the following equation:

$$\mathrm{pH}=\frac{-E+Eq-Ec}{0.05912} \text{ at } 25^\circ\ C, \tag{87}$$

where E is the observed potential, Eq is the potential of the quinhydrone-platinum electrode when $(H^+)=1$, and Ec is the potential of the saturated calomel half-cell when $(H^+)=1$. The numerical values of Eq and Ec, as given by Clark [3, p. 672], are, respectively, 0.6992v and 0.2458v, so that eq 87 becomes

$$\mathrm{pH}=\frac{0.4534-E}{0.05912}, \tag{88}$$

the sign of E being negative over most of the useful range of the electrode. Tables or charts are furnished with quinhydrone pH instruments, giving pH values corresponding to observed potentials for several temperatures.

For accurate results, the platinum or gold electrodes should be cleaned after use, and with careful manipulation the limit of error is about 0.01 pH. The quinhydrone electrode is inapplicable in the presence of oxidizing and reducing substances and in alkaline solutions with pH above 9.0. The arrangement of apparatus for pH measurements is shown in figure 59 (A).

(e) GLASS ELECTRODE

Haber and Klemenziewicz [6] appear to have been the first to demonstrate the usefulness of the glass electrode. Their electrode vessel was made by blowing a thin bulb on the end of a glass tube and contained an electrolyte in which dipped a platinum wire connected with an electrometer. The bulb was immersed in the test solution and the concentration chain was completed by means of a normal potassium chloride–calomel half-cell. The apparatus was used for electrometric titration of acids and bases, and the authors considered that the potential of the cell was determined in part by the concentration of hydrogen ions. They used a soft glass in preference to others that were tried, and directed that after the bulb was formed it was to be steamed inside and out for an hour and kept in pure water until used. Hughes [7], using apparatus similar to the above with the addition of a potentiometer, showed that the potential varies quantitatively with pH over a wide range of values and that the glass electrode may

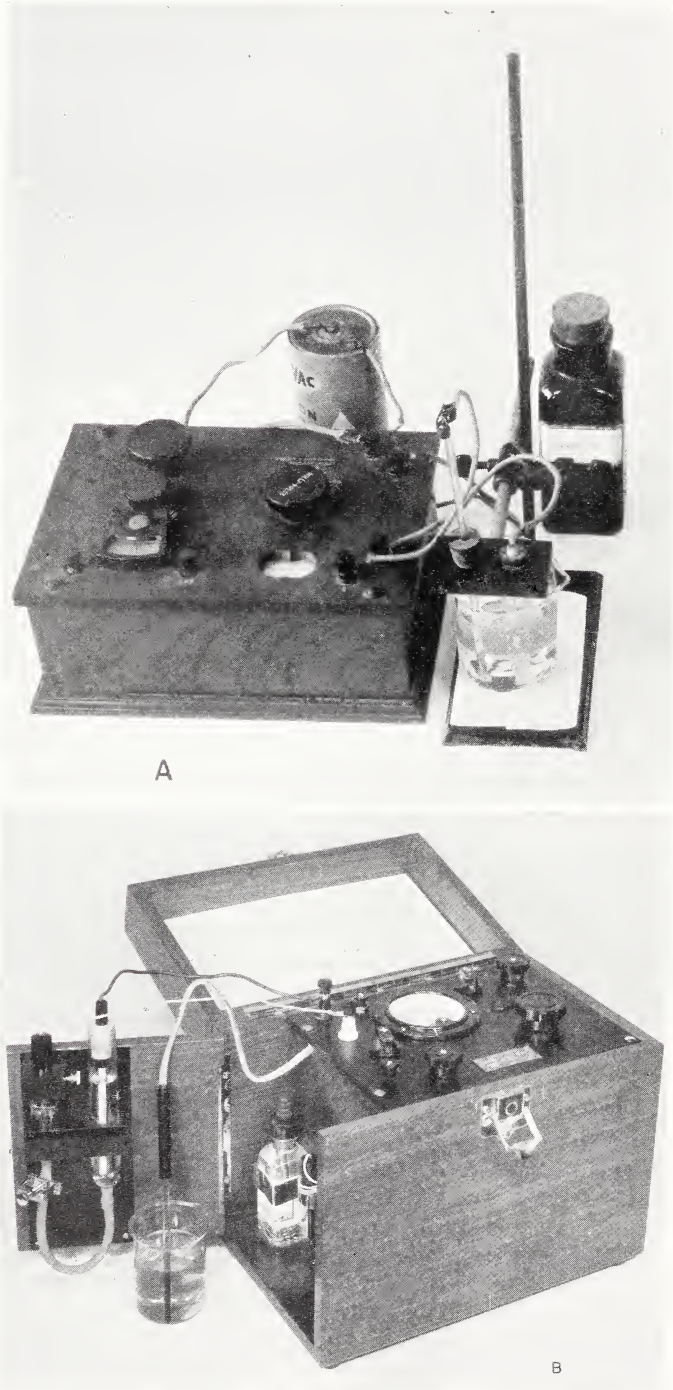


FIGURE 59.—*A, Quinhydrone potentiometer (courtesy of Leeds & Northrup Co.); B,* pH *electrometer (courtesy of Coleman Electric Co.).*

be used in the presence of strong oxidizing or reducing agents when a hydrogen electrode is useless. He also showed that the linear relationship of glass-electrode potential and pH is affected by strong concentrations of certain salts. Kerridge [8] found the glass electrode useful in the presence of substances of biological origin that poison a hydrogen electrode.

A study of the composition of glasses was made by MacInnes and Dole [9], who consider as most suitable a glass composed of 22 percent of sodium oxide, 6 percent of calcium oxide, and 72 percent of silica. Glass of this composition, known as Corning 015, is made by Corning Glass Works, Corning, N. Y. The same investigators [10] produced membranes as thin as 0.025 mm by first blowing a bubble on the end of a glass tube until red and blue interference colors appeared. The end of a second tube, heated to dull redness, is placed against the bubble and the film fused to it. These membranes are fragile but have comparatively low resistance. Robertson [11] produced thin-walled bulbs by drawing 10-mm tubing to a tapering point and forming on this a small lump of glass by heating in a pointed flame. The bulb was then blown to a volume of 8 or 10 ml. Thompson [12] devised a metal-connected glass electrode of bulb or test-tube form by silvering the outer surface. The silver film was protected by lightly copperplating and the metal coating was then wired to a potentiometer. The test solution was added to the vessel and the chain was completed by means of a saturated calomel half-cell. No standard electrolyte is used in actual pH measurement, but each electrode must be calibrated before being used. This may be done with the help of standard buffer solutions, and the cell constant is determined.

Accounts of the evolution of the glass electrode are given by Perley [13], MacInnes and Longsworth [14], and by Clark [3], while theories of the action of the electrode have been advanced by Haber and Klemenziewicz [6], Horowitz [15], Michaelis [16], Dole [17], and MacInnes and Belcher [18].

The Haber type of vessel, consisting of a thin bulb blown on the end of a glass tube, is now commonly employed. Various electrolytes have been used inside the electrode but a 0.1 N solution of hydrochloric acid (pH=1.0) saturated with quinhydrone is generally favored for routine measurements. The electrode tube is half-filled with the solution, connection with the potentiometer being made with a short length of platinum wire sealed in a narrow glass tube containing mercury into which the potentiometer lead extends. The latter tube is supported in the rubber stopper of the electrode vessel. The bulb of the glass electrode is immersed in the test solution and a calomel half-cell is used as a reference electrode. The concentration chain may be represented thus:

$$\mathrm{Hg}\left|\mathrm{HgCl,\ KCl\ (sat.)}\right|\mathrm{solution}\left|\underbrace{\left|\begin{matrix}0.1\ N\ \mathrm{HCl}\\ \mathrm{quinhydrone}\end{matrix}\right|}_{\text{glass membrane}}\right|\mathrm{Pt.}$$

The pH of an unknown solution is calculated from potential reading, E, as with the quinhydrone electrode, as described under (d), p. 289. That is, at 25° C.

$$\mathrm{pH}=\frac{0.6992-E-0.2458}{0.05912}=\frac{0.4534-E}{0.05912}.$$

Tables giving pH values corresponding to potentiometer readings at various temperatures are supplied with some instruments, whereas others are calibrated to read directly in pH values.

Since the resistance of the glass electrode is high, a sensitive detecting instrument must be used. Some workers prefer an electrometer, but with improved electrodes, a lamp-and-scale galvanometer with a sensitivity of 0.0005 μa per mm at 1 m is satisfactory, and an inexpensive potentiometer of the usual type may be used (fig. 59, A). The use of grounded metal supports for the electrodes prevents leakage currents from reaching the galvanometer.

Various methods of thermionic amplification of the weak currents of the glass electrode have been reported by Goode [19], Elder and Wright [20], Partridge [21], Müller [22], DuBridge [23], Morton [24], Gilbert and Cobb [25], and others. In figure 55 is shown a potentiometer-electrometer in which the amplification is incorporated in the potentiometer housing.

In some apparatus the entire assembly, consisting of potentiometer, vacuum-tube amplifier, dry cells, galvanometer, pH electrodes, etc., is housed in a single portable unit. One of these units is illustrated in figure 59 (*B*). With amplification, the employment of the glass electrode in automatic pH apparatus becomes possible. Longsworth and MacInnes [26] have described such a device for the automatic control of the addition of alkali solution to a growing culture of acid-forming bacteria. A pH recorder for sugar juices, in which a glass electrode is employed, is described by Crites [27].

Electrodes made of the usual glass are considered inaccurate in the presence of sodium salts at ranges above pH 9.5; however, a calibration curve may be obtained for the range 9.6 to 12.5 which is said to be reproducible within 0.1 pH. Very recently the use of a different glass suitable for high alkaline ranges, has been reported [42].

(f) SILVER–SILVER CHLORIDE ELECTRODE

The silver-silver chloride half-cell, represented by Ag|AgCl|KCl(m), where (m) refers to molar concentration, is analagous to the calomel half-cell for which it has been substituted as a secondary reference electrode, particularly in the study of reactions in chloride solutions.

The electrode consists of a coating of silver chloride, intimately mixed with silver, on platinum or silver-plated platinum. The platinum support, which may be in the form of a small rectangle of foil or gauze or a wire coil, is sealed by means of a short lead of platinum wire to a convenient length of glass tubing, as in the construction of hydrogen electrodes. The silver-silver chloride coating may be produced in various ways, either electrolytically [37], thermoelectrolytically [38], or thermally [39]. The last-named process is simple and produces satisfactory electrodes. A coil of platinum wire is sealed into a glass tube and covered with a paste composed of 7 parts of silver oxide (precipitated and washed) and 1 part of silver chlorate and heated to decomposition in an electric furnace. After coating the electrodes, regardless of the process used, they are washed in many changes of distilled water to remove contaminants, and finally washed in the solution in which they are to be used. The period of washing and aging to stability may extend to as much as 20 days.

Smith and Taylor [40] studied the reproducibility and stability of silver chloride electrodes and found an average agreement of 0.02 mv.

among electrodes produced in the several ways referred to above. They also found that even after proper aging, the potential is sensitive to polarizing currents produced by as small as 0.1 to 0.2 mv. These authors indicate that the difference in values reported for the standard potential of silver chloride electrodes, quoted as varying from 0.2221 to 0.2238 volt, may be due to insufficient aging time and consequent lack of concentration equilibrium within the porous electrode materials.

Values for the standard electrode potential of the silver-silver chloride electrode as given by Harned and Ehlers [41] for the temperatures 20°, 25°, and 30° C. are 0.2255, 0.2224, and 0.2191 volt, respectively.

The utility of the silver chloride electrode has been realized in the construction of glass electrodes where the inner member of the glass-electrode assembly is a stabilized silver chloride electrode immersed in a chloride solution, the assembly being sealed to prevent evaporation. Polarization is said to be prevented by suitable electrical construction.

3. AUTOMATIC RECORDING AND CONTROL OF pH

A scheme for the automatic recording of pH in lime-treated cane juice was described by Balch and Paine [28], wherein a tungsten-manganese sesquioxide electrode and a calomel half-cell in contact with the flowing liquid were connected with an automatic recorder. The quinhydrone electrode in special form also is used in certain industrial solutions. Reference has already been made to the employment of the glass electrode for pH control on a relatively small scale [26] and for recording the pH of sugar juices [27].

Electrodes of metallic antimony have been much used in industrial control equipment. These have the advantage of being rugged and not affected by flowing liquids. They may be set up in tanks and other vessels and used in sugar factories for both automatic recording and control of liming and gassing of beet juices. The electrode assembly consists of the antimony electrode and a saturated calomel electrode usually fitted into a chamber through which a sample of the juice flows continuously, the potential established being proportional to the pH of the juice. The electrodes are wired to a recording and controlling device which contains a potentiometer circuit in which the electrode potential is balanced automatically against an adjustable standard potential. Deviation of the pH from the control value unbalances the circuit, and the controller acting through a relay actuates a motor-drive unit, which in turn operates a feeder or valve to increase or decrease the flow of lime-milk or of gas.

The antimony electrode should be made from pure metal and depends for its action upon the presence of very slightly soluble $Sb(OH)_3$ formed by the action of dissolved air or oxygen. The exposed portion of the electrode is ground and polished at the start and is wiped clean daily. The electrodes are calibrated for the solutions in which they are to be used. The useful range of the antimony electrode under proper conditions is said to be 2.0 to 12.0 pH in continuous operation, with a limit of error of 0.2 pH. Antimony electrodes and their characteristics have been discussed by Perley [13, 29, 30]. Reference has been made in section 2 (e), p. 292, to the use of glass electrodes for pH control and recording.

4. COLORIMETRIC METHODS

(a) WITH STANDARD BUFFER SOLUTIONS

The standard buffer solutions used in the colorimetric determination of hydrogen-ion concentration, according to Clark [3], are mixtures of some acid or alkali with one of its salts, of such well-defined composition that they may be accurately reproduced, and with pH values accurately defined by hydrogen electrode measurements. Several such mixtures have been used, but the set of buffers devised by Clark and Lubs [31], as described here, have proved satisfactory and are conveniently prepared.

Stock solutions.—The following stock solutions are used in preparing the standards: 0.2 *M* hydrochloric acid, 36.465 g of HCl per liter. 0.2 *M* sodium hydroxide, 40.005 g of NaOH per liter. 0.2 *M* potassium chloride, 14.912 g of KCl per liter. 0.2 *M* acid potassium phthalate, 40.836 g of $KHC_8H_4O_4$ per liter. 0.2 *M* acid potassium phosphate, 27.232 g of KH_2PO_4 per liter. 0.2 *M* boric acid+0.2 *M* potassium chloride, one liter of the solution to contain 12.4048 g of H_3BO_3 and 14.912 g of KCl.

The ordinary chemically pure salts are not considered suitable for making these stock solutions but are to be recrystallized three or four times from water that has been redistilled from a Pyrex flask and protected from absorbing CO_2 by a soda-lime guard tube.

Although the salts, the stock solutions, and even the buffer mixtures, especially prepared for pH determination, may now be purchased, the preparation of the various stock solutions and the buffer mixtures to cover the pH range 1.2 to 10.0 is briefly outlined here. Clark's directions for recrystallizing potassium acid phthalate state that the crystallization from the hot solution should be allowed to take place slowly at a temperature not below 20° C, since there is deposited at lower temperatures a more acid salt having the form of prismatic needles instead of the six-sided orthorhombic plates of the salt, $KHC_8H_4O_4$. After the final crystallization the salt is dried at 110° to 115° C to constant weight.

Recrystallized potassium acid phosphate is dried at 110° to 115° C and potassium chloride at 120° C. The boric acid is air-dried in thin layers between filter paper, and the constancy of weight is established by drying small samples in thin layers in a desiccator over $CaCl_2$.

Preparation of 0.2 M sodium hydroxide.—To prepare the 0.2 M sodium hydroxide solution, 100 g of high-grade stick soda in a Pyrex Erlenmeyer flask is treated with 100 ml of distilled water which is used for rinsing any adhering soda from the neck of the flask. After solution and cooling, the flask is stoppered and allowed to stand until carbonate has settled. It has been found convenient to filter this strong solution by suction through purified asbestos (see Chapter XIX, 6 (a), p. 324) supported in a Jena No. 2 filter or in a Gooch crucible. From this point on, the solution is protected from absorption of CO_2 from the air by careful manipulation and by means of soda-lime guard tubes. After a rough calculation, the clear filtrate is quickly diluted to a solution somewhat more concentrated than 1.0 *M*. Of this solution 10 ml is withdrawn and titrated with an acid solution of known strength. From this standardization, the dilution required to furnish a 0.2 *M* solution is calculated. The dilution is made with the least possible exposure and the solution is poured into a bottle thickly

coated with paraffin wax and to which a calibrated 50-ml burette and soda-lime guard tubes have been attached. The solution is now carefully standardized. The purified acid potassium phthalate is recommended by Clark for this operation. Portions of the salt of about 1.6 g each are carefully weighed on an analytical balance with standardized weights and dissolved in beakers in about 20 ml of distilled water, and 4 drops of phenolphthalein are added. A stream of air free of CO_2 is passed through the solution, which is titrated with the alkali to a faint but distinct permanent pink. It is preferable to use a factor with the solution rather than to attempt adjustment to an exact 0.2 *M* solution.

Preparation of 0.2 M hydrochloric acid solution.—A high-grade hydrochloric acid solution is diluted to about 20 percent and distilled. The distillate is diluted to approximately 0.2 *M* and standardized with the sodium-hydroxide solution described above.

Preparation of the buffer mixtures.—The standard buffer mixtures used in performing the actual pH tests are made, as already indicated, by adding varying amounts of an acid or an alkali to a solution of its salt. Although in routine sugar-factory work only a limited range of buffer solutions may be required, the entire list is given here, since the occasion frequently arises for tests in other ranges.

TABLE 35.—*Clark and Lubs buffer mixtures, temperature 20° C*

50 ml of 0.2 *M* KCl+*X* ml of 0.2 *M* HCl												
Milliliters of 0.2 *M* HCl	64.5	41.5	26.3	16.6	10.6	6.7	------	------	------	------	------	------
pH	1.2	1.4	1.6	1.8	2.0	2.2	------	------	------	------	------	------
50 ml of 0.2 *M* $KHC_8H_4O_4$+*X* ml of 0.2 *M* HCl												
Milliliters of 0.2 *M* HCl	46.7	39.6	32.95	26.42	20.32	14.70	9.90	5.97	2.63	------	------	------
pH	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	------	------	------
50 ml of 0.2 *M* $KHC_8H_4O_4$+*X* ml of NaOH												
Milliliters of 0.2 *M* NaOH	0.4	3.70	7.50	12.15	17.70	23.85	29.95	35.45	39.85	43.00	45.45	47.00
pH	4.0	4.2	4.4	4.6	4.8	5.0	5.2	5.4	5.6	5.8	6.0	6.2
50 ml of 0.2 *M* KH_2PO_4+*X* ml of NaOH												
Milliliters of 0.2 *M* NaOH	3.72	5.70	8.60	12.60	17.80	23.65	29.63	35.00	39.50	42.80	45.20	46.80
pH	5.8	6.0	6.2	6.4	6.6	6.8	7.0	7.2	7.4	7.6	7.8	8.0
50 ml of 0.2 *M* H_3BO_3, KCl+*X* ml of NaOH												
Milliliters of 0.2 *M* NaOH	2.61	3.97	5.90	8.50	12.00	16.30	21.30	26.70	32.00	36.85	90.80	43.90
pH	7.8	8.0	8.2	8.4	8.6	8.8	9.0	9.2	9.4	9.6	9.8	10.0

In table 35 is shown, in the first horizontal line of figures, the number of milliliters of 0.2 *M* acid or alkali that must be added to 50 ml of a given salt solution to produce 200 ml of standard buffer mixture having the corresponding pH shown in the second line of figures.

To prepare the solutions, 50 ml of the salt solution is pipetted into a calibrated 200-ml glass-stoppered volumetric flask, and the required amount of 0.2 *M* acid or alkali is run in from a burette. The solution

is made up to 200 ml with double-distilled water, the flask is stoppered, and the solution mixed.

For storage the standard buffer solutions are transferred to resistant glass bottles labeled with the corresponding pH. The bottles containing the most frequently used standards may be provided, for convenience, with clean one-hole rubber stoppers, each carrying a 10-ml pipette.

Indicator solutions.—Indicators recommended for the colorimetric determination of hydrogen-ion determination are listed in table 36 under the common names of the dyes. The list includes the indicators originally selected by Clark and Lubs [32], while those marked with an asterisk have been added as a result of the work of Cohen [33]. All are sulfonphthaleins with the exception of methyl red, an azo dye, and cresol phthalein. Methyl red, although replaced in the revised indicator list by chlor phenol red, is included in table 36 because it is prescribed in the method of Gillespie, as described later. Opposite the name of the indicator are given the molecular weight, the number of milliliters of 0.01 N sodium hydroxide needed to form the monobasic salt of 0.1 g of dye, pK (=log $1/K$, where K is the dissociation constant of the indicator), useful pH range, and the colors of the acid and alkaline forms of the dye.

TABLE 36.—*Indicators of Clark and Lubs* [1]

1	2	3	4	5	6
Name of indicator	Molecular weight	Milliliters of 0.01 N NaOH/0.1 g of dye	pK	pH range	Color change, acid to alkaline
Meta cresol purple*	382	26.2	1.51	1.2 to 2.8	Red to yellow.
Thymol blue	466	21.5	1.5	1.2 to 2.8	Do.
Brom phenol blue	669	14.9	3.98	3.0 to 4.6	Yellow to blue.
Brom cresol green*	698	14.3	4.67	3.8 to 5.4	Do.
(Methyl red)	269	14.8	5.10	4.4 to 6.0	Red to yellow.
Chlor phenol red*	423	23.6	5.98	4.8 to 6.4	Yellow to red.
Brom phenol red*	512	19.5	6.16	5.3 to 6.8	Do.
Brom cresol purple	540	18.5	6.3	4.2 to 6.8	Yellow to purple.
Brom thymol blue	624	16.0	7.0	6.0 to 7.6	Yellow to blue.
Phenol red	354	28.2	7.9	6.8 to 8.4	Yellow to red.
Cresol red	382	26.2	8.3	7.2 to 8.8	Do.
Meta cresol purple*	382	26.2	8.32	7.4 to 9.0	Yellow to purple.
Thymol blue	466	21.5	8.9	8.0 to 9.6	Yellow to blue.
Cresol phthalein			[9.4]	8.2 to 9.8	Colorless to red.

[1] The Determination of Hydrogen Ions, W. M. Clark, 3d ed. p. 94 (Williams & Wilkins Co., Baltimore, Md., 1928).

*Added as result of later work by Cohen [33].

Stock solutions of the indicators are prepared by grinding 0.1 g of the dry powder in an agate mortar with the corresponding volume of 0.01 N sodium hydroxide given in column 3 of table 36. The alkali is added little by little, and when solution is complete it is diluted to 250 ml with distilled water to give a 0.04-percent solution. Methyl red (0.1 g) is dissolved in 125 ml. of neutral alcohol and diluted with water to 250 ml.

Performing the tests.—Test tubes 15 mm in diameter and 120 mm long are calibrated roughly for uniformity of bore by adding 10 ml of water from a pipette and choosing those in which the water stands

at approximately the same level. These are cleaned and afterward rinsed with distilled water, and drained. To separate tubes are added 10 ml. of each standard buffer mixture to cover a chosen pH range, and 5 drops of the appropriate 0.04–percent indicator solution. Meade [34] recommends that the corks used for closing the tubes be first boiled and thoroughly rinsed before inserting.

To another calibrated test tube is added 10 ml. of the solution to be tested and 5 drops of the indicator. The matching of colors is best done with the aid of a comparator, a simple form of which is the block comparator described by Clark as having six deep holes of such size as to accommodate neatly the test tubes, drilled parallel in pairs, each pair being as close together as possible without breaking the wood. Through the center line of each pair and at right angles to them are drilled three smaller holes completely through the block so that light may pass horizontally through the pairs of tubes when introduced. The block is then painted a dull black inside and out. The back of the illuminating holes is covered with a ground plate of colorless glass to diffuse the light. The sample tube with indicator is placed in one of the middle holes and backed by a tube of water. Standard tubes containing the indicator are placed in the holes on either side of the sample, and each is backed by a tube containing the sample without the indicator, thus compensating for color and turbidity in the sample. When the sample appears to fall midway between two standards that differ by 0.2 pH unit, let us say, for example, between pH 7.2 and pH 7.4, then the value 7.3 may be taken as the pH of the sample.

There are other forms of comparators arranged for quick and convenient exchange of color standards, such as that of Meade and Baus [35], which has a sliding rack carrying alternate tubes of color standard and water, and of such length as to cover the entire pH range of the indicator. A metal cover with suitably spaced apertures, and having sockets for holding tubes of the sample and the sample plus indicator, is provided. A white surface at 45° is placed behind the apertures and illuminated from above with a Daylite Mazda bulb.

Care must be exercised in maintaining like volume of solutions and of indicators and like thicknesses of light-transmitting layer. Alkaline and neutral buffer solutions should be protected from absorbing carbon dioxide and should not be allowed to come in contact with the hands.

(b) WITHOUT BUFFER SOLUTIONS—GILLESPIE METHOD [36]

This method for the determination of hydrogen-ion concentration without the use of buffer mixtures depends upon the ratio of the number of drops of a given indicator present in a solution wholly transformed into the alkaline form to the number existing wholly in the acid form.

The indicators used are those of the original selection of Clark and Lubs [32]. The stock solutions of the dyes are prepared, except in the case of methyl red, by grinding 0.1-g portions with 1:1 equivalents of alkali solution (1.5 equivalents in the case of cresol red) to give the monosodium salt of the indicator acid. The equivalents of sodium hydroxide may be obtained from table 36, column 3. When the dye is in solution the volume is made up to 250 ml with water. Methyl red is dissolved as explained under (a), p. 296.

In determining the data upon which table 37 is based, Gillespie

made use of the Clark and Lubs buffer mixtures, as given in table 35, which were checked electrometrically. The data were then smoothed by use of the equation pH$=k$ log (alkaline form)/(acid form), where pH is the hydrogen-ion exponent, k is the apparent or total dissociation constant of the dye, and "alkaline form" and "acid form" designate, respectively, the concentrations of the indicator completely transformed into the alkaline or acid form by excess of base or acid. In table 37 the drop ratios are given in the first column, the first figure of the ratio being the alkaline form and the second figure the acid form of the dye. The pH values corresponding to these ratios are found in the succeeding columns headed by the indicator used.

TABLE 37.—pH *values corresponding to various drop ratios* [1]

Drop ratio	Brom phenol blue	Methyl red	Brom cresol purple	Brom thymol blue	Phenol red	Cresol red	Thymol blue
1:9	3.1	4.05	5.3	6.15	6.75	7.15	7.85
1.5:8.5	3.3	4.25	5.5	6.35	6.95	7.35	8.05
2:8	3.5	4.4	5.7	6.5	7.1	7.5	8.2
3:7	3.7	4.6	5.9	6.7	7.3	7.7	8.4
4:6	3.9	4.8	6.1	6.9	7.5	7.9	8.6
5:5	4.1	5.0	6.3	7.1	7.7	8.1	8.8
6:4	4.3	5.2	6.5	7.3	7.9	8.3	9.0
7:3	4.5	5.4	6.7	7.5	8.1	8.5	9.2
8:2	4.7	5.6	6.9	7.7	8.3	8.7	9.4
8.5:1.5	4.8	5.75	7.0	7.85	8.45	8.85	9.55
9:1	5.0	5.95	7.2	8.05	8.65	9.05	9.75
Produce acid color with.	0.05 N HCl, 1 ml	0.05 N HCl, 1 drop	0.05 N HCl, 1 drop	0.05 N HCl, 1 drop	0.05 N HCl, 1 drop	2% H_2KPO_4, 1 drop	2% H_2KPO_4, 1 drop

[1] L. J. Gillespie, J. Am. Chem. Soc. **42**, 744 (1920).

The following is the Gillespie procedure for the preparation and use of the color standards: Test tubes, preferably without flanged tops, 15-mm bore and 150-mm length, selected for uniformity of bore as already described under (a), are cleaned, rinsed, and drained. The tubes may be held in pairs by means of a rubber band wound around them in the form of a figure 8. It is convenient to use test-tube racks, one for each indicator, each holding two rows of tubes, accommodating one tube of each pair in front and one in back. For any desired indicator a set of color standards is prepared by placing from 1 to 9 drops in the back row of tubes, and 9 to 1 drops in the front row. A drop of 0.05 N sodium hydroxide is then added to each of the tubes in the back row (2 drops in the case of thymol blue) to develop the alkaline color. A 0.2-percent solution of stick soda is sufficiently accurate for this solution. To each of the tubes in the front row is added the kind and quantity of acid indicated at the bottom of each column in table 37. According to Clark, the 0.05 N hydrochloric acid is prepared with sufficient accuracy by diluting 1 ml of concentrated hydrochloric acid (sp gr 1.19) to 290 ml. The volume is at once made up in all the tubes to a constant height, corresponding to 5.5 ml with distilled water. Each pair of tubes thus constitutes a colorimetric standard and is to be labeled with the corresponding pH value given in table 37. These dilute standards are not considered stable and daily renewal is recommended.

A block comparator for matching solutions and standards, as shown in Gillespie's article, is illustrated in figure 60. This is a modification of the comparator described in section (a) in that there are three holes in series instead of two to accommodate the extra tube. A third series of vertical holes with a third observation hole would permit comparison with two adjacent standards in the indicator range.

To perform a test, 10 drops of the desired indicator solution is added to a clean test tube, and the test solution is added in amount to match the height of the standard solutions in their tubes. The sample tube with the indicator is placed in the comparator and is backed by two tubes containing distilled water. Pairs of the indicator tubes are placed in two of the holes of the other series and are backed by a tube containing the sample without the indicator. For colorless test solutions, one compensating tube may be omitted from each series. The pH value of the pair of standards most nearly matching the sample containing the indicator is taken as the pH value of the sample. The same precautions pointed out in the previous section are to be observed in regard to volume and concentration relations.

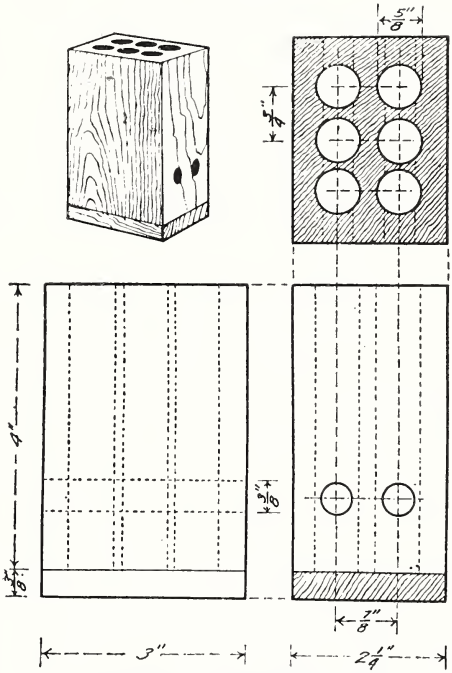


FIGURE 60.—*Comparator for* pH *measurement (after Gillespie).*

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XIX COLORIMETRY

1. INTRODUCTION

The maintenance and improvement of the quality and appearance of sugar products leads naturally to the recognition of the importance of colorimetry and of the need for adequate apparatus and methods for the measurement of sugar color. The early literature on this subject dealt with methods used in connection with the refining of sugar with bone char; thus Ventzke [1] in 1860–61 published the description of a "decolorimeter," by means of which colors of solutions were compared before and after char treatment. In these articles Ventzke referred to the work done by Payen about 25 years previously. In 1861 Stammer [2] published a description of the instrument and method for sugar colorimetry that bears his name, and which, little changed, is still in use.

In 1873 von Vierordt studied the measurement of color in diluted molasses with a spectroscope, the entrance slit of which was divided into upper and lower halves by independent jaws actuated by micrometer screws. To each screw was attached a drum which bore a graduated scale reading from 0 to 100. The opening and closing of the slits thus served to vary the light intensity in a measurable manner in either half of the field of view. The description of this apparatus is contained in a reprint in the Bureau's possession. This was reprinted in 1873 by Schmidt & Haensch, Berlin, from an article by Vierordt, but the journal source is not cited. The table in the reprint gives $-\log$ transmittancy corresponding to scale readings, and layer thickness and dilution were taken into consideration in the text, the latter on a volumetric basis. This approach to a spectrophotometric method apparently received little attention from sugar technologists until many years later.

In 1920 Bates and Associates [3] published a description of an abridged spectrophotometer (to be described later) with which three pure spectral lines of the mercury arc were used. This was the beginning of a systematic investigation of color in sugar products at the National Bureau of Standards. Spectral-transmission and absorption curves of a large number of varied sugar products were obtained over a greater part of the visible spectrum [4] and these afforded a qualitative and quantitative measure of sugar color and its characterization, and a way to the scientific classification of sugar products according to color. These results served as a basis for further investigation and demonstrated the possibility of using abridged spectrophotometric methods and simplified apparatus whereby sugar colorimetry, on a spectrophotometric basis, was made quite as simple as by the Stammer method and without the objectionable features of the latter.

In 1936 the International Commission for Uniform Methods of Sugar Analysis [5] at its London meeting unanimously adopted the resolution that " * * * spectrophotometry is to be considered the basis of all colorimetric measurements in the sugar industry. It is therefore recommended that absolute measurement be introduced as far as possible into factory and commercial control, the measurements to be performed with the monochromatic light of the mercury arc, namely at the wave lengths 4358, 5461, and 5789 A, and that measurements of $-\log \mathbf{t}$ at 5600 A be calculated from the measurements at 5461 and 5780 A. It is to be understood that any country or group of workers may use other wave lengths as desired."

The adoption of the above resolution was prompted by practical, as well as theoretical considerations. Not only is the measurement of absorption more exact with monochromatic illumination than with white light as used in former days, but it is much easier for the observer, and there seems to be no other means of interrelating such measurements over the whole gamut of sugar color. Spectrophotometric equipment has been in use for several years in many laboratories in the sugar industry for purposes of research and control and this use is increasing, particularly in the field of simplified or abridged spectrophotometry adaptable to routine observations.

2. COLOR NOMENCLATURE IN THE SUGAR INDUSTRY [4]

In the work at the National Bureau of Standards on color phenomena in sugars, the recommendations contained in the various reports of the Committee on Standards and Nomenclature and of the Progress Committees of the Optical Society of America have been adopted. Special care has been taken to conform to the recommendations of the Committee on Spectrophotometry [6, 7] and of the Committee on Colorimetry (Preliminary Draft) 1919, and subsequent reports of this latter committee published from time to time, insofar as those recommendations adequately cover the ground. In certain cases, however, it has been found necessary to coin new terms and symbols. Where this has been necessary, the new symbols and terms have been selected and defined in such a manner as to cover the desired ground and at the same time be an extension of, and not

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in conflict with, the recommendations contained in the committees' reports.

To one not thoroughly familiar with the subject, the elaborate and extensive system, with its fine distinctions of meaning to be hereinafter set forth, may appear somewhat pedantic and academic. Not so, however, to him whose daily work is in this field, for he is continually inconvenienced and annoyed by the circumlocution and misunderstandings occasioned by lack of suitable terms and symbols to express his ideas and findings cogently and without ambiguity.

It will be noted in the list of terms below that there are many that are not explicitly used in the color work on sugar products. The terms that are most used in experimental sugar work are relatively few in number ($\mathbf{T}$, $\mathbf{t}$, $-\log \mathbf{t}$, $-\log t$, c, b, λ, Q, n, as defined below). The others are necessarily given for the purpose of precisely defining these terms and to bring out the small but important differences between them and certain other similar terms.

In the case of homogeneous light passing through homogeneous substances, such as a plane parallel polished plate of glass, we have the following terms [6], all being functions of wave length:

E=radiant energy (of light source).
E_1=radiant energy incident upon the first surface.
E'=radiant energy reflected at the first surface.
E_{I}=radiant energy transmitted by the first surface.
E_2=radiant energy incident upon the second surface.
E''=radiant energy reflected at the second surface.
E_{II}=radiant energy transmitted by the second surface.
$E_{\mathrm{I}}=E_1-E'$.

$T=\frac{E_{\mathrm{II}}}{E_1}$=transmission. It is the fraction of the incident light which is transmitted, and not lost either by reflection or absorption.

$\mathsf{T}=\frac{E_2}{E_1-E'}=\frac{E_2}{E_{\mathrm{I}}}$=transmittance; that is, the transmission after correcting for losses by reflection [8, 9]. The transmittance per unit of thickness, which is called transmissivity, t, may be calculated from the transmittance, T, for any thickness, b, by means of the relation

$t=\sqrt[b]{\mathsf{T}}$=transmissivity, which is known as the Lambert law. No exceptions to this law have ever been noted.

$\mathsf{A}=1-\mathsf{T}$=absorbance.

For transparent solutions:

$T_{\mathrm{soln.}}$=transmission of a given cell containing the solution.

$T_{\mathrm{solv.}}$=transmission of the same (or a duplicate) cell containing pure solvent.

$\mathbf{T}=\frac{T_{\mathrm{soln.}}}{T_{\mathrm{solv.}}}=\frac{\mathbf{T}_{\mathrm{soln.}}}{\mathbf{T}_{\mathrm{solv.}}}$=transmittancy; that is, the transmission after correction for reflection at the surfaces and for absorption, if any, by the pure solvent.

Since the absorption of pure water is negligible for our purposes, $\mathbf{T}$ has practically the same significance as T above. The symbols $\mathbf{T}$, $\mathbf{t}$, $\mathbf{A}$, referring to solutions, are distinguished from T, t, A, referring to solids (or homogeneous substances), in handwriting and typewriting by underscoring the former, and in printing by the use of

bold-face type as is recommended in the spectrophotometry report (J. Opt. Soc. Am. and Review Sci. Instr., February 1925). Since in all cases we compensate for losses by reflection by the use of a water cell (or one containing a colorless sucrose solution) exactly similar to the cell containing the solution to be measured, we have to do only with the transmittancy, **T**, and not at all with the transmission, T, or the transmittance, T.

t=specific transmissivity=transmittancy reduced to unit conditions as regards thickness and concentration; **t** differs from t above in that **t** takes into account concentration as well as thickness.

b=thickness (cm) of the absorbing solution.

c=concentration (grams of saccharine dry substance per 1 ml of solution). c refers exclusively to the original colored dry substance, which consists of sucrose+nonsugar+coloring matters.

$$\mathbf{t}=\sqrt[cb]{\mathbf{T}} \text{ or } -\log \mathbf{t}=\frac{1}{cb}(-\log \mathbf{T})=\text{(Lambert-Beer law).}^{13}$$

$-\log$ **t** is a measure of the coloring power—that is, intensity of absorption—of the unknown amount of coloring materials associated with 1 g of saccharine dry substance.

$$\mathbf{A}=1-\mathbf{T}=\text{absorbancy.}$$

Since the transmissivity, t, and the absorption coefficient or exponent are related according to the equation $t=e^{-i}$, where i, the absorptive exponent, depends upon the nature of the substance and the wave length, it is evident that independent of the original use of the minus sign before the log t (log transmissivity) as a matter of convenience, $-\log t$ is the absorptive index and has a definite physical significance.

$-\log$ **t**=the specific absorptive index.[14]

λ=wave length.

One color degree is the integrated (sum total) effect for the visible spectrum of one absorption "unit" at each wave length. One unit of coloring matter evokes a color sensation of one color degree and is measured by its integral (sum total) absorption $\left(\sum_{\lambda=440}^{\lambda=700} -\log \mathbf{t}_1\right)$

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[13] This law may or may not be valid for different types of coloring matters in solution under the conditions obtaining in the sugar industry. Under these conditions it is valid at best only within rather narrow confines as to concentration and transparency. However, it was found to be valid for several hundred absorption spectra of technical sugar products ranging from white sugar to final molasses, but only upon condition that stable transparency was produced in the solutions. This was accomplished by an improved process of colorimetric clarification, which is described below.

[14] $-\log$ **t** in the above committee reports was defined as specific transmissive index instead of absorptive index. That specific absorptive index is the more appropriate name may be seen from the following demonstration. Using the symbols tabulated above for a homogeneous solid, suppose a beam of light passes through a parallel-faced slab of thickness, b. The change (decrease) in energy, E, of the beam in passing through the nfinitely thin layer, db, is given by the differential equation, $-dE=iEdb$, where i is a coefficient proportional to the absorption or absorbing power of the substance. It depends upon the nature of the substance and the wave length, but is constant for any given substance at any given wave length. It may be called the absorption coefficient or exponent, as will appear later.

Separating the terms of this equation we have $-(dE)/E=idb$. Integrating between the limits $b=0$ to $b=b$ and $E=E_1$ to $E=E_2$ as above defined, we have

$$-\log_e E\Big]_{E_1}^{E_2}=ib\Big]_0^b$$

Putting in these limits, $-[\log_e E_2-\log_e E_1]=ib$, or $-\log_e E_2/E_1=ib$. Since $E_2/E_1=\mathsf{T}$, $-\log_e \mathsf{T}=ib$, or $i=-1/b \log \mathsf{T}=-\log t$. Therefore, $t=e^{-i}$. Since i in the differential equation is the quantity which defines absorption, $-\log_e t=i$ should be called the absorptive exponent and $-\log_{10} t=i/2.3026=k$ should be called the absorptive index.

over the visible spectrum. The visual effect of this is represented by $\sum_{\lambda=440}^{\lambda=700} VE\mathbf{t}$ the luminosity curve of the transmitting layer of unit thickness.

n=the number of units of coloring matter corresponding to n color degrees and n absorption units.

$$n=\frac{-\log \mathbf{t}_{\lambda=560} \text{ (of sample)}}{-\log \mathbf{t}_{1\lambda=560} \text{ (of standard)}}=\frac{-\log \mathbf{t}_{\lambda=560} \text{ (of sample)}}{0.00485}.$$

The sum total absorption of one unit of coloring matter, $\sum_{\lambda=440}^{=700} -\log \mathbf{t}_1$, is defined as equivalent, colorimetrically, to the common absorption unit, $-\log \mathbf{t}_1$, measured at $\lambda=560$, the wave length at the optical center of gravity of its luminosity curve. The numerical value of $-\log \mathbf{t}_1$ at $\lambda=560=0.00485$.

n is the number of units of coloring matter in 1 g of saccharine dry substance.

3. VISUAL SPECTROPHOTOMETRIC APPARATUS

Reports on spectrophotometry and descriptions of spectrophotometers have been published by the Committee on Spectrophotometry of the Optical Society of America [6], and later Gibson [9] described several spectrophotometers and discussed factors affecting the reliability of spectrophotometric data. McNicholas [10] has described in detail some of the equipment for routine spectral transmission and reflection measurements used at the National Bureau of Standards. Description and illustrations of various instruments are to be found also in catalogs and advertising literature issued by the makers.

A spectrophotometer is a combination of devices consisting of (1) a spectrometer for breaking up the light from the source into its constituent wave lengths, (2) a photometer for securing a two-part photometric field with means for varying the brightness of one or both parts in a measurable manner so that the eye is enabled to judge equality of brightness, and (3) a source of light with auxiliary equipment such as sample cells, supports, etc. With such apparatus, transmission measurements may be made at numerous points over the entire visible spectrum, and from the data curves may be plotted and various ratios calculated which permit qualitative and quantitative comparison of sugar color.

There are also simpler instruments not equipped with a dispersing device but arranged by other means whereby certain wave lengths or narrow spectral bands are made available for limited or abridged spectrophotometry. Such instruments are well suited to routine work in technical laboratories and are described in this section.

(a) BAUSCH & LOMB SPECTROPHOTOMETRIC EQUIPMENT

The Bausch & Lomb spectrophotometric equipment as used principally for sugar colorimetry at the National Bureau of Standards is described here to exemplify one type of polarization instrument. In the drawings shown in figure 61 (Bausch & Lomb booklet [11]) the sections are, respectively, plan and side view of the complete assembly for transmission measurements at fixed thickness, and a

large-scale view of the Martens-type photometer. The lettering of the parts is uniform throughout. Light from the lamp, L_1, is diffused by the double-ground glass, L_2, which becomes the source of illumination. The beams are collimated and directed by the wedges, A, and

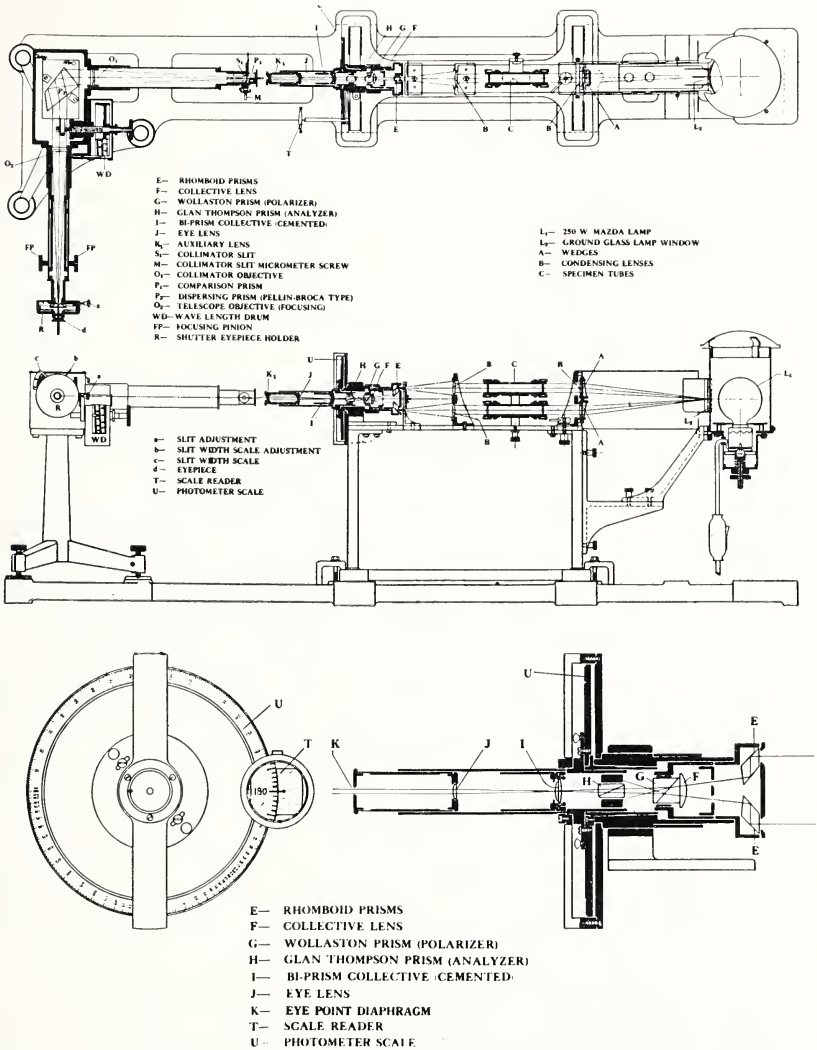

FIGURE 61.—*Bausch & Lomb spectrophotometric outfit for transmission measurements.*

Above, plan and side view of complete assembly; below, large-scale view of photometer.

lenses, B, through the solution and solvent cells, C, and are focused by the second pair of lenses, B, upon the rhombs, E, at the aperture of the photometer whereby they are directed through lens, F, into the polarizer, G, a Wollaston double-image prism. The two beams, one from each aperture, transmitted by the Wollaston prism are polarized

in mutually perpendicular planes and enter the analyzer, *H*, a Glan Thompson prism fixed in a rotatable sleeve to which is attached the graduated circle, *U*. By rotation of the analyzer the intensities of the two beams may be equalized and the angle of rotation noted on the circular scale. The light of the two beams transmitted by the analyzer is focused upon the biprism at *I*, whereby it is directed along the axis of the photometer. On leaving the analyzer, the light of these two beams is linearly polarized in the same plane, so that the action of the biprism on each beam is the same.

At the eyepiece diaphragm, *K*, may be seen a circular field with horizontal dividing line formed by the edge of the biprism which is brought into focus by means of lens, *J*. By rotation of the analyzer through 360°, it is seen that complete extinction of each half of the field occurs twice at points 90° apart. Midway between each pair of extinctions lies a point at which the two halves match. This is the zero point. When the instrument is in proper adjustment and both apertures are equally illuminated, the zero point falls at 45° and the photometer becomes direct reading.[15] One quadrant of the circle is calibrated to read directly in terms of *T*, a second quadrant in terms of −log percent, and the remainder of the circle in degrees from 0° to 180° C.

The eyepiece diaphragm at *K* is replaced by a short-focus lens that images the photometric field upon the adjustable vertical collimator slit of the spectrometer at *S* in the focal plane of the collimator lens, O_1. Spectrally dispersed by the prism, P_2, the light enters the telescope system through the objective, O_2, and is observed through the eyepiece lens at *d*. Within the eyepiece holder, *R*, is a shutter or eyepiece slit, the width of which is adjustable by lever *b*, thus defining the length of the spectral band observed and controlling the spectral purity. The eyepiece slit is movable horizontally across the axis of the telescope and along the length of the spectrum by turning screw head *a*, which provides a means of wavelength calibration. The dispersing prism is mounted on a turntable actuated by a micrometer screw to which the wavelength drum, *WD*, is fixed. The latter is graduated in units of 1 mμ, from 400 to 800 mμ. The rotation of the prism table brings any desired part of the spectrum upon the central part of the field as defined by the ocular slit and as indicated on the wavelength drum. At the eyepiece lens of the spectrometer the observer sees a rectangular field composed of two juxtaposed spectra with horizontal dividing line; in other words, a portion of the spectral image of the two-part photometric field.

The wave-length scale of the spectrometer may be calibrated by means of mercury or helium lamps, or by wave lengths from other sources. The photometer scale may be checked by means of rotating sectors of fixed opening (see following section) [10], which may be accurately calibrated mechanically, or by means of filters of accurately known transmission [9]. Measurements on a solution at different thicknesses may also assist in detecting errors, the negative logarithm of the transmittancy being accurately proportional to the thickness [9].

[15] In earlier designs of the Martens photometer, the biprism was cemented to the front face of the Wollaston prism. The light of the transmitted beams, being polarized in planes mutually perpendicular, was affected unequally by the inclined faces of the biprism, and the amount of light transmitted by the two halves of the biprism was not the same. The zero point, therefore, did not fall at exactly 45°, which precluded the use of direct reading.

A pair of absorption cells to contain solution and solvent, respectively, are shown at C. The diameter of these should be such that light does not reach the inside cylindrical surfaces and become reflected into the photometer. This, however, may be prevented by using proper diaphragms. The focusing lenses at *B*, nearest the photometer, may be omitted in many cases or may be replaced with a diaphragm, thus allowing longer absorption cells to be used. To permit measurements over a wide range of transmission and long spectral range, an assortment of matched pairs of cells should be available in thicknesses between end plates of 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 cm. The 0.5, 1.0, and 2.0-cm sizes are available in the usual U-shaped form with glass separators, while the larger sizes are in the form of glass cylinders fitted with screw caps in the manner of saccharimeter tubes and having stoppered side openings. Cells with fused-on glass end plates may now be purchased.

The interchange method is used in measuring the transmission of a solution relative to that of the solvent at any wave length. After a series of measurements has been recorded, the position of the cells relative to each other (and to the respective apertures of the photometer) is reversed and a second series of an equal number of readings is taken. If either of the direct-reading scales has been used, the arithmetic mean of all the readings is taken as $\mathbf{T}_\lambda$ or $-\log \mathbf{T}_\lambda$. If the degree scale is used with the zero point falling at or near 45°, the arithmetic mean of each series of readings in angular degrees is taken and the transmittancy is found by

$$\mathbf{T} = \cot \theta_1 \times \tan \theta_2, \tag{89}$$

where θ_1 and θ_2 are the observed angles of match, respectively, with the sample in positions 1 and 2.

By the use of an illuminated white-lined sphere substituted for *L*, the apparatus may be used for spectral-reflection measurements. The reflection standard and the sample are in a rotary specimen holder in a vertical position at the side of the sphere opposite the apertures of the photometer and are illuminated by the white inner surface of the sphere which contains two 500-watt Mazda lamps. Soft sugars may be pressed into a suitable container in a manner to present a smooth, flat surface, the reflectance of which may be measured. For dry granular sugars a cover must be used to retain the sample because of the vertical mounting. According to Judd and Gibson [56], an error of as much as 10 percent may result from the use of the cover glass.

(b) GAERTNER POLARIZING SPECTROPHOTOMETER

This apparatus, figure 62, also consists of a spectrometer, polarizing photometer, illuminating device, and equipment for mounting the samples [12].

The white-lined diffusing sphere at the right contains four 200-watt incandescent lamps and serves for illumination. For transmission measurements, a diffusing white surface is placed at the back of the sphere and serves as the light source (upper drawing). This may be replaced by an opal or ground glass, if desired, permitting illumination by a mercury arc or other source. Light from the diffusing surface is collimated by a lens and then divided by a pair of rhombs into two

beams that pass through the tubes containing the solution and solvent. The beams are then directed by rhombs and lenses into the Martens-type photometer.

For reflectance measurements (lower part of diagram) the first pair of rhombs is removed, the two beams coming directly from the surfaces of sample and reference standard. The sample and standard are carried on a holder and may be interchanged in vertical position. This position is not suitable for dry, granular sugars.

The photometric field is circular with horizontal dividing line, being projected through the entrance slit to a position in the collimator objective where it is viewed from the ocular slit without eye lens. Transmission and reflectance are computed by the formulas used with the instrument described under (a), p. 307. The instrument also

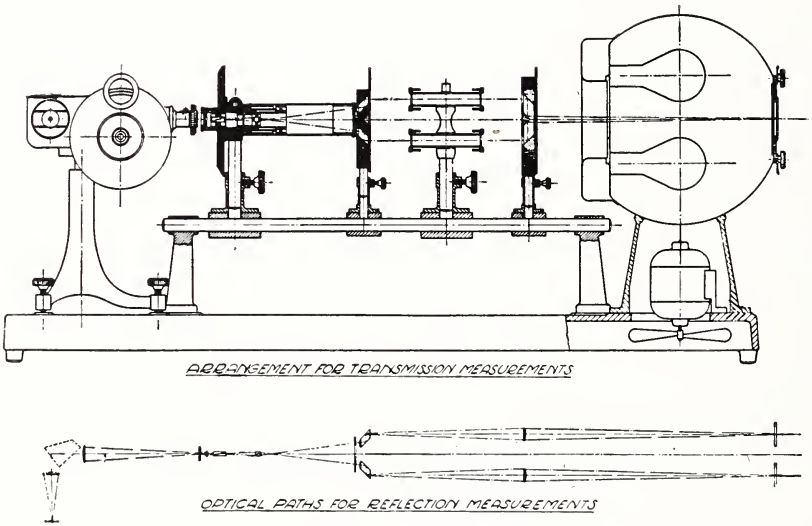

FIGURE 62.—*Gaertner polarizing spectrophotometer.*

may be made direct reading if the angle of match (100 point) can be secured at exactly 45°.

(c) KÖNIGS-MARTENS SPECTROPHOTOMETER WITH AUXILIARY EQUIPMENT DESIGNED AT THE NATIONAL BUREAU OF STANDARDS

The following description of this apparatus is a part of that given by Gibson [9], and figure 63 is a reproduction of figure 3 of an article by McNicholas [10].

Light entering the collimator slits, *A* and *B*, forms beams 1 and 2. These beams follow the usual course through the collimator lens, dispersing prism, and telescope objective. Cemented to the latter lens is a combination of Wollaston prism, wedge, and biprism. The purpose of the wedges in the collimator and telescope is to prevent passage to the eye of certain multiply reflected rays from the optical surfaces.

Looking through the ocular slit one sees the surface of the biprism uniformly illuminated by a mixture of light of wave-length range determined by the widths of the collimator and ocular slits, the mean wave length corresponding to the position of the ocular slit in the spectrum. The biprism edge forms a vertical dividing line in this photometric field which is circular and the lights in the two halves of the field are plane-polarized in directions perpendicular to each other.

By turning the nicol between the eye and the ocular slit, the two parts of the field may be matched in brightness.

For spectral-transmission measurements three different illuminants are used, viz, the mercury arc, the helium lamp, and the incandescent lamp. Only the latter is shown in the diagram. Each of the three illuminants is mounted in a small enclosure, the inside surface of which is coated with MgO. In each case the light used for the transmission measurements is taken from the diffusing rear surface of the enclosure; this is collimated by the combination lenses (3) and enters the collimator slits, *A* and *B*, as shown.

The drum in which the analyzing nicol is mounted is graduated only in degrees reading from 0° to 360°. Since the angle of match does not fall exactly at 45°, the scale is not direct reading. The method of interchanging the sample in the two beams is used, and **T** is computed by formula:

$$\mathbf{T} = \cot \theta_1 \times \tan \theta_2.$$

The mercury and helium illuminants afford ready means of checking the wave-length calibration of the spectrophotometer; they also enable measurements of

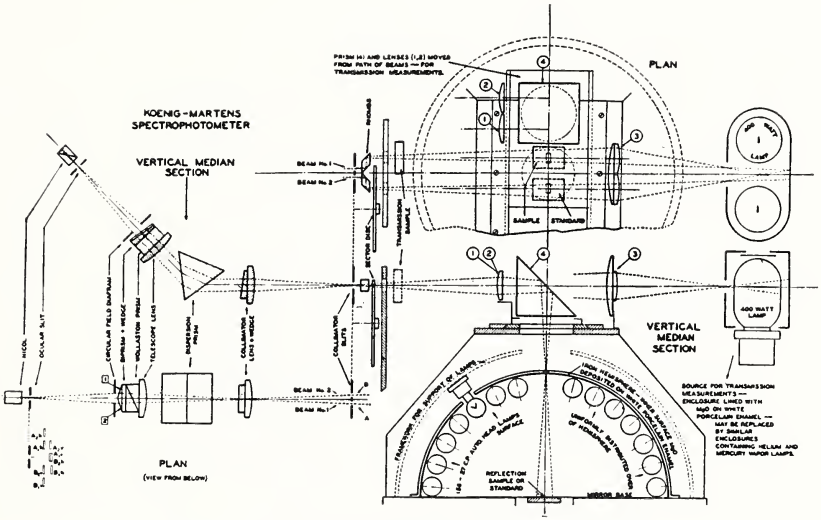

FIGURE 63.—*Königs-Martens spectrophotometer.*

transmission to be made at certain wave lengths free from slit-width or wave-length error.

The rotating sector, shown in the diagram between the collimator slit and the transmission sample, serves two purposes: (1) It enables a direct check to be made on the reliability of the photometric scale. A number of sectors are available to give transmissions of approximately 0.01 to 0.80. These apertures are accurately determined mechanically. Any desired sector may be placed in position, rotated rapidly enough to eliminate flicker, and its transmission determined photometrically in the same manner as for the transmission sample. (2) To measure low transmissions, the 0.10 or 0.01 sector is placed in the blank beam and the transmission of the sample is measured relative to that of the sector. This brings the angles of match away from the extinction points into a more suitable region of the scale and greatly extends the range of the instrument for low transmission measurements.

For spectral reflectance measurements, the sample and reference white standard are placed, as shown, at the base of a hemisphere whose interior surface is coated with MgO and studded with 156 small lamps so that, in effect, the sample and standard are in completely diffused illumination. The light reflected at right angles from the sample and standard, respectively, forms beams 1 and 2 and enters the spectrophotometer via right-angled prism 4 and lenses 1 and 2. Sample and standard may be reversed in position by the observer and the apparent

reflectance of the sample, R_s, relative to that of the standard, R_0, is given by the relation, analogous to formula 89,

$$\frac{R_s}{R_0} = \cot \theta_1 \tan \theta_2.$$

(d) KEUFFEL & ESSER COLOR ANALYZER

This spectrophotometer is designed for both transmission and reflectance measurements and the arrangement of parts and the light paths are shown in figure 64, as given in the article by Keuffel [13]. The white-lined sphere is illuminated by two 400-watt lamps. For transmission measurements, two blocks of magnesium carbonate are placed at 6 and 7. The light diffusely reflected from these surfaces is incident upon the cells at 8, containing solution in the upper one and

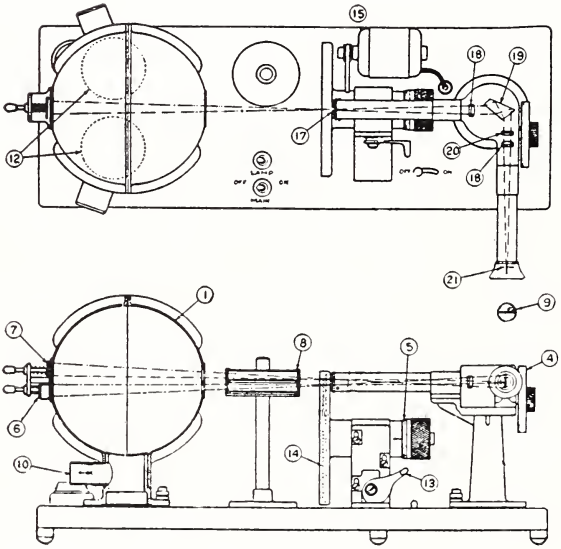

FIGURE 64.—*Keuffel & Esser color analyzer.*

Upper, plan; lower, side view. 1, White-lined sphere; 4, wave-length scale; 5, photometer scale; 6, magnesia block; 7, magnesia block or solid sample; 8, cells for solution and solvent; 9, two-part field; 12, lamps; 14, revolving sectors; 15, motor; 17, entrance slit; 18, collimating lens; 19, dispersing prism; 20, lens; and 21, eyepiece diaphragm.

solvent in the lower. The photometric device consists of two sectored disks, one larger in diameter than the other, encased in a housing, 14, with windows through which the light passes to the slit. These disks rotate around the same axis in the same direction and are driven by a motor at sufficient speed to eliminate flicker. The smaller sector is movable concentrically across the openings of the larger while rotating, by means of the knurled head to which the photometer scale, 5, is attached. Near its edge the larger sector, intercepting the upper beam in which the solution is placed, transmits a constant amount of light which enters the upper half of the collimator slit of the spectrometer. The combined opening of the two sectors below the edge of the smaller intercepts the lower beam transmitted by the solvent, the amount of light entering the lower half of the slit being variable from 0 to 110 percent.

The spectrometer is similar to that already described in (a) and (b). Wave-length selection is accomplished by turning the knob attached to the wave-length scale, 4. The emergent spectra from the dispersion prism are directed along the telescope tube and are viewed through the ocular slit, 21, where a circular 2-part field with horizontal dividing line is seen. The two halves of the field may be matched by turning the knurled head carrying the photometer scale and the transmittancy is read directly. The lever at 13 operates an adjustment which lowers the sectors and doubles the amount of light transmitted. This arrangement is used for low transmissions, the sectors being so constructed that the scale then reads four times the actual value.

4. APPARATUS FOR ABRIDGED SPECTROPHOTOMETRY

(a) IVES TINT PHOTOMETER [14]

This instrument, which has been widely used in the sugar industry, is illustrated in figure 65. Light from the Daylite lamp located at

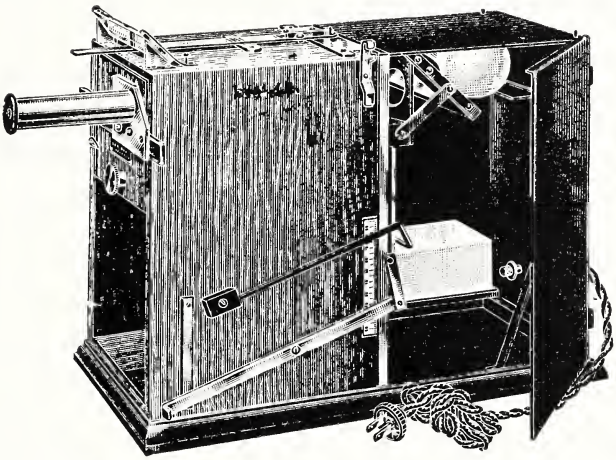

FIGURE 65.—*Ives tint photometer.*
Courtesy of Palo-Meyer.

the back near the top is diffusely reflected upward by the block of $MgCO_3$ that rests on an adjustable support and is again reflected by the inclined mirror into the two entrance apertures of the instrument. The width of one aperture is fixed, while the width of the other may be varied measurably by a lever shown at the top of the instrument. The index on this lever traverses a scale graduated to read from 0 to 100 in equal divisions corresponding to the percentage of opening. At a reading of 100 the two halves of the eyepiece field should match. Three color filters (red, green, and blue) supplied with the instrument permit measurements to be made in the three corresponding spectral regions. A fourth filter, transmitting a rather broad band of yellow green, is provided for the use of sugar technologists. Between the mirror and the apertures, provision is made for placing absorption cells. To make a measurement, the cell containing solution is placed over the fixed aperture, while the cell with solvent is placed

over the variable aperture. With a chosen color filter in place, an intensity match is obtained by means of the lever, and the scale reading is noted.

A mercury-arc light source with appropriate spectral filters, as described under 5 (e) p. 324, may be used to advantage with the Ives Tintometer, or a Brewster or Gibson filter may be used for direct measurement at λ560 mμ (see 4, (c), p. 314).

Meade and Harris [15] evolved a method for translating the scale readings of the Ives Tintometer into sugar color units. They obtained transmittancy readings with different concentrations of a certain raw sugar in water solution and found that any set of readings in a series is related according to a power function such that where

y=any scale reading,
K=the scale reading for 1 unit of material, and
x=the number of units of material required to give a scale reading of y,

then

$$y=K^x, \text{ or } \log y=x \log K, \text{ from which } x=\frac{\log y}{\log K}.$$

To avoid repeating the calculation for each reading, Meade and Harris adopted the reading 99 as a standard and calculated a table by means of the last expression, wherein is given for each scale reading, y, the corresponding number of color units, x, of the hypothetical solution (K=99).

(b) MODIFIED STAMMER COLORIMETER

Bates [16] and associates [3] first used the mercury arc as a light source for sugar colorimetry in connection with a modified Stammer colorimeter. The arrangement of the apparatus is shown in figure 66. A sector is mounted on a shaft which rests on bearings in such position that, when rotating, the blades of the sector alternately intercept and transmit the beam of light entering the open tube of the colorimeter. When the speed of rotation is high enough to eliminate flicker, the light transmitted is directly proportional to the aperture of the sector, which may be determined mechanically. Two such sectors are used, one transmitting 80 and the other 46 percent, and are easily interchangeable on the shaft. The shaft is provided with a pulley connected to the small driving motor by a belt.

The column of solution in the closed colorimeter tube is varied in length by means of the plunger until the intensities of the two halves of the field match. The height of the liquid column, in centimeters, is read on the scale. The transmittancy, **T**, is then equal to the known T of the sector, from which $-\log$ **t** is calculated by $-\log \mathbf{t}=1/cb\ (-\log \mathbf{T})$.

The reflection losses caused by the end plates in the solution tube and plunger are compensated by introducing two similar plates over the upper end of the open tube.

Spectral filters for isolating the yellow, green, and blue-violet mercury lines are described under 5 (e), p. 324.

(c) DUBOSCQ COLORIMETER

A standard type of Duboscq colorimeter has been adapted by Brewster [17] to purposes of abridged spectrophotometry suitable for

sugar factory laboratories. The light source may be either a mercury arc with the appropriate filters or an incandescent tungsten lamp with which a special 560-mμ filter is used. Glass plates calibrated for transmission at the various wave lengths are used as standards. The apparatus, figure 67, consists of a Bausch & Lomb Duboscq colori-

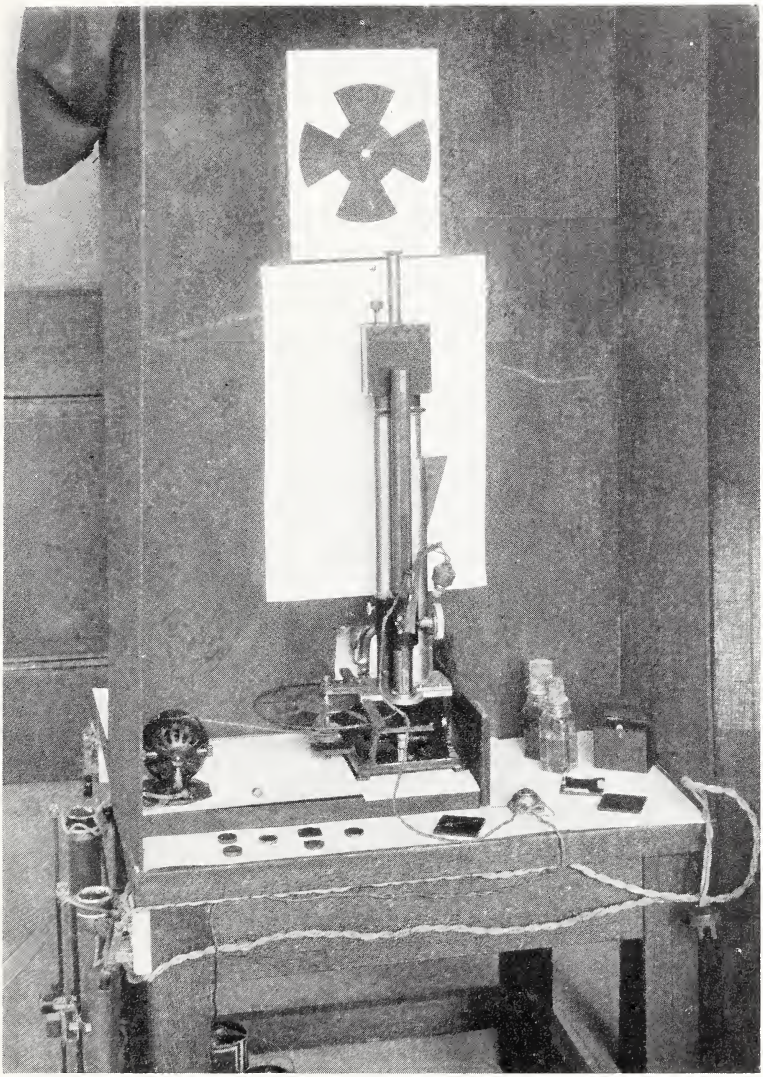

FIGURE 66.—*Stammer colorimeter modified for abridged spectrophotometry.*

meter with 10-cm cups, to the vertical column of which a shelf with a heavy bracket is fastened with screws to leave a clearance of 1 cm when the cups are in their lowest position. A carrier for the standard plates with a 25-mm center orifice, and with the ends cut as shown, slides between guides on the shelf and has a slot that engages in a

metal stop at the center of the shelf to center properly the orifice under either cup. A 60° prism enclosed in the triangular housing of the eyepiece telescope permits observation with the head in a natural, unstrained position. The adjustable mirror at the bottom of the colorimeter is silvered glass with the outer surface ground to diffuse the reflected light.

Spectral filters for obtaining light from ordinary tungsten illumination at wave length 560 mμ or close thereto have been devised by Brewster [18] and by Gibson [19]. These permit very satisfactory measurement of transmittancy at this wave length. The composition of these filters is given in table 38.

TABLE 38.—*Spectral filters for 560 mμ*

Brewster		Gibson	
Material	Thickness	Designation of glass	Thickness
			mm
Wratten filter 21	1 layer	Corning 351	4.55
Wratten filter 61	do	Corning didymium 512	5.82
Corning didymium glass 512	6.5 mm	Jena VG—3	1.99
Colorless glass	1 to 2 mm	Jena BG–18	1.94

The components are sealed together with Canada balsam and may be bound with black tape or mounted in metal. The filters may be cut to such diameter as to be mounted in the telescope tube of the instrument or may be used over the eyepiece. In the Brewster filter the gelatine sheets are sealed between the glass components. In the Gibson filter the Jena glasses are sealed between the Corning components.

In the Brewster filter the spectral centroid of the transmitted light for incandescent tungsten illumination at 2,848° K was computed to be 558.8 mμ. For the original Gibson filter and certain replicas made at this Bureau, the optical centroid, under the same conditions as above, was found to be located at 560.0 mμ.[16]

A second filter consisting of a blue glass, Jena BG–12, thickness 3.42 mμ, is used by Brewster for the special case of very pale sugar solutions, such as those of high-grade refinery products. The optical centroid of this filter was computed for 2,848°K as being at 459.9 mμ.[17]

The photometric standards are plane parallel plates of polished glass, the color of which is known as "carbon amber." This glass is obtainable in shades varying from brown to palest straw. These are to be calibrated in terms of transmission, T, at wave length 560 mμ. This calibration is best obtained by sending the plates to the National Bureau of Standards with a request for calibration, as above specified.

The transmission value may be controlled by the shade and thickness of the glass, and it is advisable to have plates of three values.

[16] At the time this was written there was difficulty in obtaining exact duplication in the two Jena glasses used in the Gibson filter. However, it is doubtful that a slight shift of the optical centroid on either side of λ560 by 1 or 2 mμ would greatly affect the results in sugar colorimetry. Attempts to duplicate this filter by substituting glasses with transmission properties too greatly different from those specified by Gibson would likely result in an inferior filter.

[17] In order to measure transmittancy in extremely pale sugar solutions at 560 mμ, excessive layer thickness is required beyond the 10 cm available in the standard type of Duboscq colorimeter. Employment of the 460-mμ filter is therefore a compromise between having an instrument constructed with much longer cells or choosing a wave length at which the light absorption is greater.

one each with $T_{\lambda=560\ m\mu}$ about 50, 70, and 80, respectively. This makes for flexibility of the method, permitting measurements over a sufficient range of shades. The glass is customarily supplied in the form of 2-inch polished squares, but other shapes and sizes may be specified to conform to the construction of the instrument. For measurements with pale solutions and the 460-mμ filter, a plate consisting of colorless optical glass calibrated in terms of T at 460 mμ is used.

To measure the transmittancy of a solution a portion is added to each colorimeter cup, a standard is placed in the carrier and centered under one of the cups, which is adjusted in height to a scale reading of 1 cm. With the spectral filter in place, the observer adjusts the height of the opposite cup to a photometric match and records the scale reading. Three to five such settings are made, and the standard is shifted by sliding the carrier and centering the standard under the opposite cup, which is then adjusted to the 1-cm scale reading as above, and a second series of the same number of readings is recorded. This substitution method of comparison is the usual one employed with direct-reading spectrophotometers and serves to compensate for any error of zero setting.

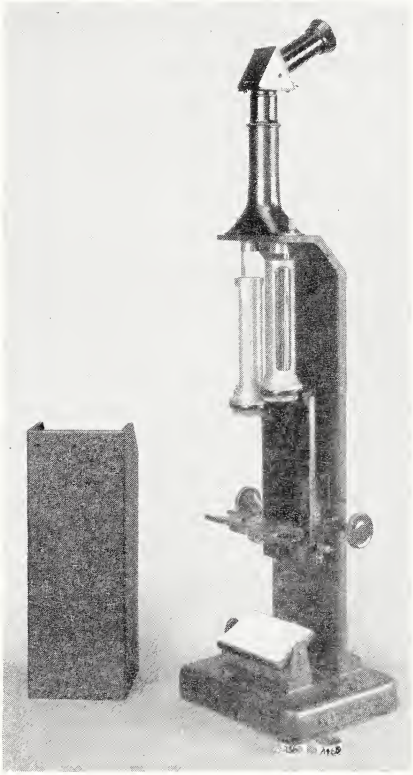

FIGURE 67.—*Duboscq colorimeter with accessories for abridged spectrophotometry.*

The readings in centimeters are added, and the sum is divided by the total number of readings to give the mean. The blank setting (1 cm) is deducted, and the remainder represents that thickness, b, of the solution whose transmittancy, **T**, equals the calibrated transmission of the standard at the specified wave length. Assuming that the dry substance concentration, c, in grams per milliliter, as given in table 114, (corresponding to the refractometric Brix of the solution) is already known, the final value, $-\log$ **t**, is found by substituting the values of b, c, and $-\log$ **T** (table 129) in the Lambert-Beer equation, $-\log \mathbf{t} = 1/cb\ (-\log \mathbf{T})$.

(d) ZEISS-PULFRICH PHOTOMETER

This instrument, with accessories and methods of manipulation for various photometric purposes, was first described by Pulfrich [20]. The diagram in figure 68 illustrates the photometer (accessories not shown). The optics will be understood from a glance at the drawing.

It consists in principle of two parallel telescopes having a common eyepiece, and is enclosed in a cast housing. The device for measurably varying the intensity of the light is shown in the drawing.

The two diaphragm leaves, with 90° openings, are movable toward or away from each other by equal amounts by means of the micrometer screws. These screws are turned by means of the drum upon which scales are engraved. When the drum is set at the scale-reading 100, the diaphragm is full open; and at 0 (a complete drum revolution) it is completely closed. One scale reads directly in values of transmission and the other in extinction ($-\log T$). The graduations are read from a common index line engraved on a small glass plate. Since both telescopes are provided with photometric devices, the substitution method may be used. The instrument may be mounted either in a vertical or a horizontal position. Supports, absorption cells, and illuminating lamps with appropriate housing, including a mercury-vapor lamp, are available. The Zeiss pamphlet [21] describes these in detail.

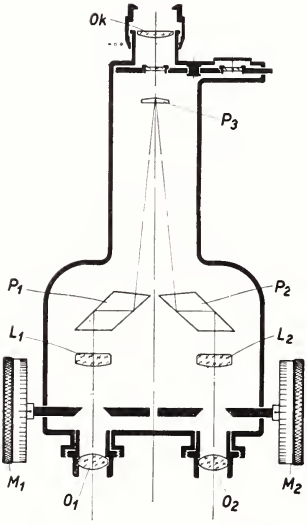

FIGURE 68.—*Zeiss - Pulfrich photometer (schematic section).*

O_1, O_2, Object lenses; M_1, M_2, photometer drums with scales; L_1, L_2, lenses; P_1, P_2, prisms; P_3, biprism; *Ok*, ocular lens.

Four different kinds of color filters designated *S*, *K*, *L*, and *Hg*, respectively, are supplied for use with the photometer, the *Hg* series being used with the mercury arc, and the others with incandescent tungsten or other white-light source.

There are nine filters in the *S* series characterized by high optical density and narrowest transmitted spectral band of the three series. The seven filters of the *K* series transmit relatively wider bands and more light than the *S* series, while the three *L* filters have high transmission and are used for faint luminosities. Landt [22] states that the Pulfrich photometer with a mercury arc as light source, and with the appropriate spectral filters, may be recommended for purposes of color measurement in the sugar industry. No doubt one of the 560-mμ filters described under (c) p. 314 could be used to advantage with this instrument.

5. PHOTOELECTRIC PHOTOMETERS

Photoelectric cells of various kinds have become available at moderate cost within the past few years, and their use in the construction of colorimetric apparatus has become widespread. This is true particularly in the field of analytical chemistry, a review of which, with an extensive bibliography, has been published by Müller [23]. The advantages and limitations of photoelectric cells in colorimetry have been discussed by Gibson [24].

Among the advantages of photoelectric over visual methods may be named: Greater objectivity of measurement; relief from eyestrain and fatigue; and, under good conditions, greater speed. The precision and

reliability of results depend upon the design and construction of the apparatus. Specific literature references to the measurement of sugar color with certain photoelectric instruments are given in references [25 to 33] at the end of the present chapter. Some of the instruments there cited had been designed primarily for sugar colorimetry, while others evidently were intended for purposes of analytical chemistry. For the measurement of transmittancy of sugar solutions over a great range, as, for example, in comparing the decolorizing efficiency of carbons, a flexibility is demanded that is not usually present in analytical apparatus. This may be attained by providing for (1) the accommodation of a variety of thicknesses of absorbing layer up to 20 cm and (2) for the employment of monochromatic light. The second of these considerations is more important in photoelectric than in visual photometry over wide transmission ranges, because when a photocell is illuminated by a spectral band that is too wide, it responds to all the impinging light, whereas the eye, being unable to integrate over a broad spectral band, responds to the effective wave length.

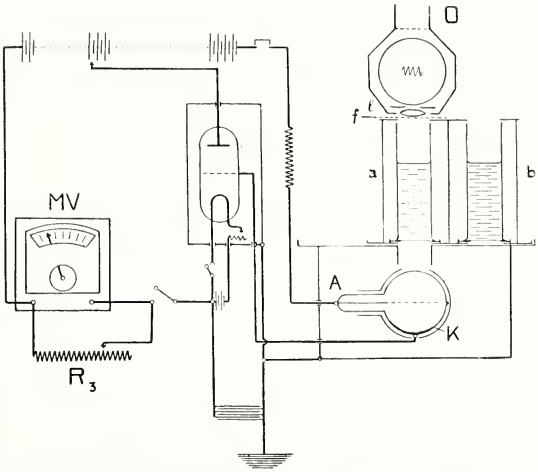

FIGURE 69.—*Objective sugar colorimeter of Sandera.*

Discussion of the numerous optical and electrical arrangements that have been employed in the construction of photoelectric photometers cannot be attempted here. This is to be found in the references cited. The instruments described in the following pages have been used particularly for the measurement of sugar color and will serve to illustrate some principles of design and construction.

(a) SANDERA OBJECTIVE SUGAR COLORIMETER [25]

The apparatus devised by Sandera is illustrated in figure 69. Light from the incandescent filament inclosed at *O* passes through the diaphragm and lens at *e* to form a practically parallel beam, which is transmitted by the solvent in cell, *a*, or solution in cell, *b*. These cells rest upon a movable carrier, whereby the cells may be interchanged as desired. The transmitted beam enters the window of the phototube, *A* (a potassium cell) and strikes the sensitive surface, *K*. The voltage is supplied from a battery. The photoelectric current is amplified by means of the vacuum tube, while the millivoltmeter in the plate circuit is the indicating instrument. By means of the variable resistance, R_3, the sensitivity of the millivoltmeter may be varied so that dark- and light-colored solutions may be measured equally well.

323414°—42——22

Color filters are introduced at f. The voltage of the light source may be regulated either by means of an iron resistance or manually by means of a rheostat and voltmeter.

The null, or "dark," current on the millivoltmeter, always present in this apparatus, is designated as e_0. To obtain the transmittancy of a solution the cell containing the solvent is placed in the light beam and the reading, e_1 is noted. The cell containing the solution is next exposed and the reading, e_2, noted. Then $\frac{e_2-e_0}{e_1-e_0}=\mathbf{T}$, from which $-\log \mathbf{t}$ is calculated.

(b) HIRSCHMÜLLER APPARATUS

This instrument was first described briefly by Landt and Hirschmüller [29] and later in greater detail by Hirschmüller [34] in a Beer's-

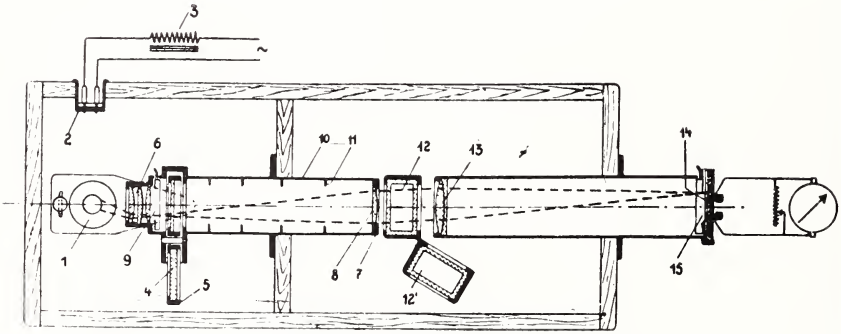

FIGURE 70.—*Hirschmüller photoelectric colorimeter.*

1, Mercury arc; 2, plug connector; 3, reactance; 4, spectral filter; 5, filter holder; 6, three-part condenser; 7, fixed aperture; 8, lens; 9, variable aperture; 10, tube; 11, diaphragms; 12 and 12', cells for solution and solvent; 13, achromat; 14, photocell; and 15, iris diaphragm.

law study of beet sugars. Details of construction of the photometer and of the Multiflex galvanometer are shown diagrammatically in figures 70 and 71.

As shown in figure 70, the light source at 1 is a high-pressure mercury arc operating on a 180- to 250-volt alternating current. An inductance, 3, limits the current to 1.3 amperes. Fifteen minutes after starting the lamp it burns with full intensity and with little change in voltage. The emitted light consists of a weak, continuous spectrum, which is disregarded, and a number of intense lines of the mercury spectrum, the ultraviolet portions of which are absorbed by the glass of the lamp. The wanted visible lines are isolated by means of colored-glass filters analogous to those described under (e), p. 324. The filters, held in the revolving holder, 5, are readily changeable. The absorption cells, up to 5 cm in length, at 12 and 12′, rest on a revolving platform controlled by a knob above the housing and are thus interchangeable. The light beam, defined by properly arranged lenses and diaphragms, reaches the selenium barrier-layer photocell with minimum divergence.

The response of the photocell to various light intensities is measured by means of the Multiflex galvanometer of Lange [35], illustrated diagrammatically in figure 71. The distinguishing feature of this

galvanometer is that the image of the straight lamp filament is reflected by the galvanometer mirror and by fixed strip mirrors over the paths represented by the broken lines to the 20-cm scale of the ground-glass window at 5. The working distance of 1 meter is thus attained in a relatively small housing. Using a pair of matched absorption cells in the manner already described, the transmittancy of a solution, **T**=deflection solution/deflection solvent, is obtained for any of the three wave lengths.

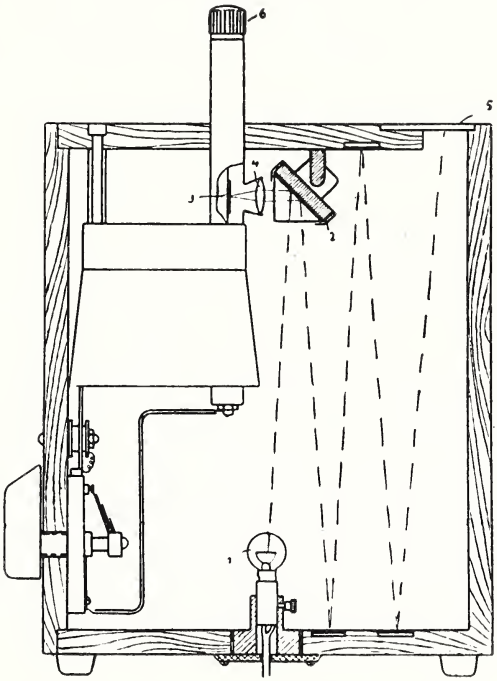

FIGURE 71.—*Multiflex galvanometer of Lange.*
1, Lamp; 2, prism; 3, galvanometer mirror; 4, lens; 5, scale; and 6, adjusting knob.

(c) COMPENSATING VACUUM PHOTOTUBE PHOTOMETER

The apparatus described below is a modification of the photoelectric colorimeter of Withrow, Shrewsbury, and Kraybill [38] and is used at the National Bureau of Standards for the measurement of transmittancy in sugar solutions. Either a mercury arc with appropriate filters, or a Mazda lamp with a 560-mμ filter, may be used interchangeably as a light source. The optical bench accommodates absorption layers up to 20 cm in thickness and the measuring bridge is simplified. The phototubes may be operated from either 115-volt alternating- or direct-current, the latter being the more satisfactory. The apparatus is illustrated schematically in figure 72, and by figure 73.

The light source is at *S*. The mercury arc used is a vertical quartz Uviarc, 22.5 cm over-all in length and 1.8 cm in diameter, giving an arc about 7.5 cm in length. The lamp is fixed to the door of the lamp housing, which is hinged so as to open downward. By lowering the door, the mercury flows to the tungsten anode and the arc is struck when the door is replaced. At either side, and close to the lamp, are metal diaphragms with 12.5-mm openings. Fins on the diaphragms aid in disseminating heat. The lamp housing is ventilated by openings at the back and a cover with a chimney may be used. On either side of the source, the instrument is symmetrical except for the absorption-cell carrier, which is placed on the right side of the instrument.

On either side of the light source are lenses at L_1 placed so that the source is in their focal planes, and at L_2 are long-focus lenses, placed so that an image of the Mazda filament is focused on the surface of the cathode of the phototube. The diaphragms covering these lenses have 12.5-cm openings. Between each pair of lenses is a 4-cm absorption cell containing a solution of $CuSO_4.5H_2O$, 45 g per liter, to remove infrared and visible red from the mercury spectrum. Shorter cells may be used and would require proportionately greater concentration of the salt. In the large compartment at the right is a sliding brass plate with two shallow grooves, as indicated, in which are placed cylindrical absorption cells, one for the solution and the other for the solvent. Either of these may be brought into the light beam, as

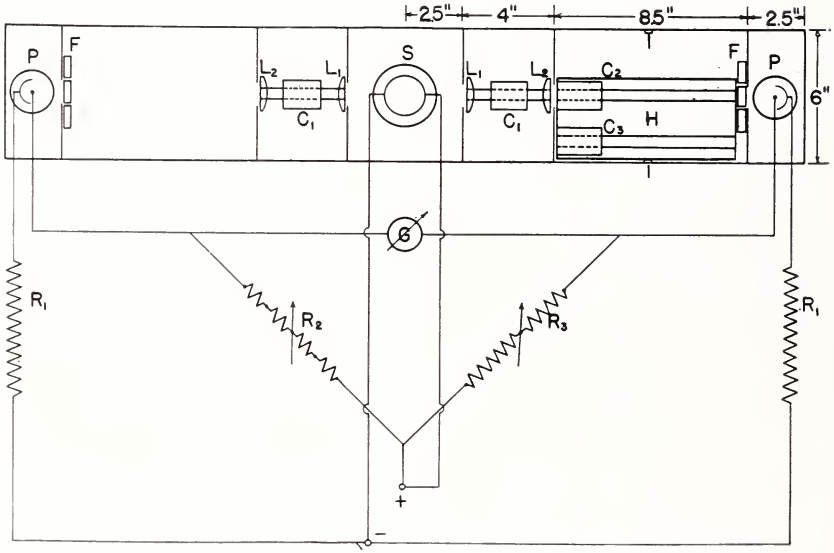

FIGURE 72.—*Phototube photometer used at National Bureau of Standards for sugar solutions.*

desired, by means of the rod, R. The glass spectral filters are mounted in blocks, F, in which are corresponding openings admitting the light to the phototube. The latter are cesium oxide vacuum cells supplied by the Continental Electric Co. When covered, the metal compartment serves as light and electrical shielding. The whole is built upon a bed plate of 0.5-inch pressed steel, which in turn rests on three steel bars, each having a leveling screw at one end. The cover is sheet aluminum connected to ground.

The phototube may be operated from the 110-volt supply, direct or alternating current, the cathodes or light-sensitive surfaces being connected to the negative terminal of the direct current supply or to ground through the 25,000-ohm resistors. The anodes or electron collectors of the phototubes are connected through the ratio arms of the bridge to the positive terminal of the voltage supply.

The arm at the right consists of two wire-wound radio rheostats in series, the nominal resistances of which are 10,000 and 1,000 ohms, respectively. These are for coarse and fine adjustment in calibration.

The ratio arm at the left is a Leeds & Northrup four-dial decade resistance box, range 1 to 10,000 ohms, and is used for the measurement. The null instrument is a type *R* Leeds & Northrup lamp and scale galvanometer, No. 2500, with *b* suspension, rated sensitivity, 0.0005 μa/mm.

To perform a measurement of transmittancy, the arc is struck and allowed to burn during 10 minutes to reach full intensity. At the same time the current is turned into the phototubes, which are allowed also to "warm up." A pair of matched absorption cells, of proper thickness, with plane parallel end plates, and thoroughly cleaned, are chosen. One is filled with the solution to be tested and the other with the solvent. With the pair of spectral filters to give the desired wave length in each beam, the solvent cell on the carriage is centered in the beam at the right, and with the dials of the resistance box set to read 10,000 ohms, the galvanometer scale reading is brought

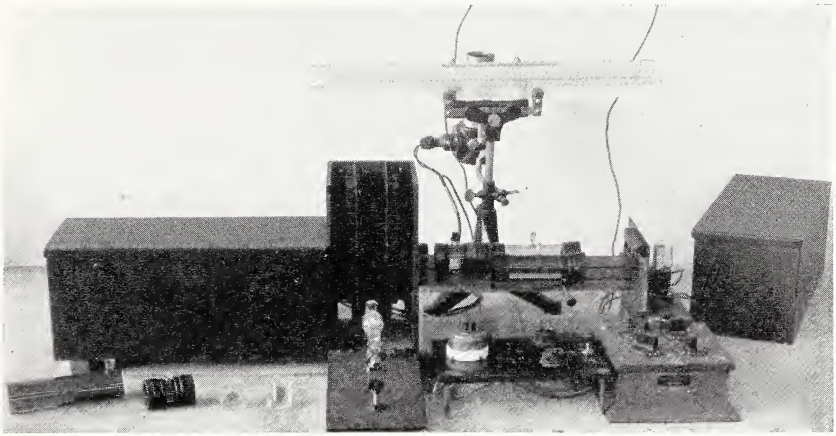

FIGURE 73.—*Phototube photometer, showing mercury arc, absorption tube, and other accessories.*

to zero by turning the rheostat knobs. By means of the 1,000-ohm rheostat this may be done exactly. The galvanometer switch is thrown off and the solution cell is centered in the beam. The galvanometer is switched on and the scale reading is brought to zero by means of the resistance box. The dial reading is then the transmittancy, **T**, of the solution. With the galvanometer well-protected against vibration, these measurements may be exactly duplicated. The galvanometer is sensitive to dial settings in the fourth figure under favorable conditions of illumination, but accurate readings in the third place are sufficient.

For routine quantitative measurements of sugar color, a 200-watt Mazda projection bulb is used along with the special filters for 560 mμ described in section 4 (c), p. 314. These filters may be set in the blocks to replace a pair of the mercury-arc filters.

(d) KEANE AND BRICE SUGAR PHOTOMETER

This apparatus was designed primarily for the industrial grading of white sugars on the basis of (1) the appearance of a sugar in terms of

its reflectance for white light, (2) the apparent color of an unfiltered solution in terms of its transmittancy for red and green light, and (3) the turbidity of the solution in terms of its transmittancy for red light. Since the color filters used transmit very wide spectral bands, the results obtained are not related to those obtainable with a spectrophotometer, but are peculiar to the photocell-filter combination. The following description of the instrument is condensed from the article of the authors [28]. The optical arrangement of the photometer is shown schematically in figure 74 and the wiring diagram is figure 75.

A beam of light from a 50-watt projection lamp, *J*, passing through a color filter, *F*, is made parallel by lens, *L*, and is divided by a clear-glass plate, *A*, roughly 10 percent of the light being reflected onto the "compensating" photocell, P_2, while the main beam passes through a compartment containing an absorption cell, *C*. After reflection by a mirror, *M*, the collimated beam strikes the standard white reflecting surface, *S*, at an angle of 45°, and a cone of diffusely reflected light is

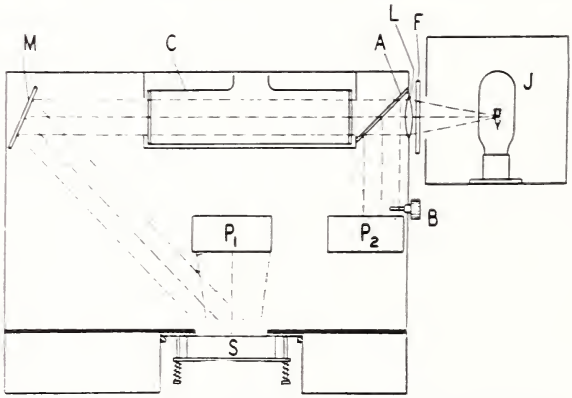

FIGURE 74.—*Photoelectric photometer of Keane and Brice.*

received by the "measuring" photocell, P_1, placed directly above and with its sensitive surface parallel to the standard reflecting surface. A sliding shutter operated by screw, *B*, provides a means of making small adjustments in the light intensity received by P_2. The parts, *F*, *C*, and *S*, are mounted on slides and can be withdrawn from the light beam or replaced as required.

The diagram in figure 75 illustrates the compensating photoelectric circuit of the apparatus. P_1 and P_2 are photronic cells in a parallel connection with a 22-ohm mirror galvanometer, *G*, of sensitivity 0.36 μa/mm and a 35-ohm precision-wound, 12.5 cm diameter Leeds & Northrup potentiometer rheostat, *R*. The uniform scale of the latter is calibrated from 0 to 100. The conditions under which the scale indicates light transmission or reflectance include (1) suitable photocells, (2) a low resistance value for the potentiometer rheostat, and (3) moderate illumination of the photocells.

For reflectance measurements, the granulated sugar is poured into a metal dish 63 mm in diameter and 16 mm deep and the top surface is carefully smoothed until it is flush with the edge of the dish. Slight overfilling or underfilling will cause appreciable error, since the distance from the reflecting surface to the photocell is only 55 mm. The

reflectance standard is an opaque white glass plate with a finely ground surface having a reflectance of 0.856 relative to that of a freshly prepared magnesium oxide surface measured in place in the instrument. With the standard white plate in position in the light beam, the galvanometer is adjusted to read zero, the rheostat scale set to 85.6, the lamp turned on, and the shutter, *B*, moved until the galvanometer again reads zero. The standard plate is then replaced by the sugar sample by moving the slide. The galvanometer deflects and the circuit balance is restored by adjusting the rheostat. The scale reading then indicates the reflectance of the sample relative to magnesium oxide. A comparison of readings made by the authors for individual samples indicated the necessity of screening the sugars to uniform grain size.

For transmittancy measurements, a 150-g sample of sugar is dissolved in distilled water at room temperature and, without filtering is made up to 250 ml. The solution, free from air bubbles, is transferred to a 150-mm absorption cell with plane parallel end plates.

A reference cell, similar to, but only half as long as, the solution cell, is also filled with distilled water. The reasons for using the 75-

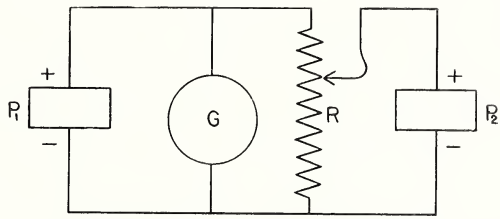

FIGURE 75.—*Compensating photoelectric circuit of Keane and Brice.*
P_1, Measuring photocell; P_2, compensating photocell; *G*, galvanometer; *R*, potentiometer rheostat.

mm solvent cell are: (1) The sugar solution used contains only 51.2 percent of water; (2) water of this depth appreciably absorbs red light beyond about 690 mμ with a maximum absorption at 760 mμ; and (3) the red filter used, freely transmits light absorbed by the water, and the photronic cell shows appreciable response to radiation in this part of the spectrum. One starts with the 75-mm cell of water in the light beam and, with the standard white plate in position, the scale is set to read 100. After the circuit is balanced by turning screw *B*, the water cell is replaced by the 150-mm solution cell and when the circuit is balanced by means of the rheostat, the scale indicates the transmittancy of the solution. The transmittancies are measured first with a blue-green filter (Corning light shade blue-green, No. 428, 3.4 mm thick) and then with a red filter (Corning traffic red No. 245). The *apparent color index* is then computed from the ratio of the transmittancies by the formula

$$I_c = 100\left(1 - \frac{\mathbf{T}_g}{\mathbf{T}_r}\right)$$

and the *index of turbidity* by the formula

$$I_t = 100(1 - \mathbf{T}_r).$$

Turbidity measurement is further considered in chapter XX,* p. 341.

* Nees, [32] using a Lange photoelectric colorimeter [35], determines color and turbidity in the unfiltered solution with blue and yellow filters. The apparatus is first calibrated by reading the relative percentage of absorption of blue and yellow light by a given unit of color and turbidity. From this relationship both color and turbidity are calculated and expressed as the percentage of absorption of blue light.

(e) MERCURY-ARC SPECTRAL FILTERS

The mercury arc is useful, not only for the wave-length calibration of spectrometers, but because the intense light of three lines of the mercury spectrum may be isolated in sufficient purity by means of properly selected filters. It constitutes an admirable light source for abridged spectrophotometry of sugar solutions, as indicated above. Spectral filters for this purpose may be composed either of colored glasses, single and in various combinations, or of dyed gelatine film properly mounted. The composition of various glass spectral filters is to tbe found in the paper by Gibson, Tyndall, and McNicholas [8], and in the catalog of Corning Glass Works entitled "Glass Color Filters." The filters given in table 39 have been used both in visual photometry and with the photoelectric apparatus described under (c), p. 319. It is to be emphasized that when photoelectric cells are used, high spectral purity is essential, and since all of the filters transmit more or less red and infrared, this radiation must be removed from the radiation reaching the photocell. This may be done by interposing a water solution of copper sulfate of such thickness and concentration that the number of grams of $CuSO_4.5H_2O$ per liter is equal to 178 divided by the length of the cell in centimeters. For visual photometry the red may be removed by means of Corning Dark Shade Blue-Green No. 430, 4 mm thick. In table 39 are given the mercury wave length isolated, the designation of the glass components, the thickness, and the transmission of each of the filters of this particular set at the wave length isolated. There is also included a list of dyed gelatine filters under the manufacturer's designation. These are described in the catalog of the Eastman Kodak Co., Rochester, N. Y., under the title Wratten Light Filters. These filters also transmit some visible red.

TABLE 39.—*Mercury-arc spectral filters*

Wave length	Glass filters			Wratten filters
	Designation of Corning glass	Thickness	T	Filter number
mμ		*mm*		
435.8	Blue Purple Ultra, 585	3.98	22.5	50
	Noviol A, 038	1.89		
546.1	Yellow Shade Yellow, 351	2.50	61.5	77 or 77 A
	Didymium, 512	6.00		
578 (576.9, 579.1)	Red Shade Yellow, 348	6.00	41.0	22

6. FILTER AIDS AND FILTRATION OF SOLUTIONS

(a) PREPARATION OF ASBESTOS [39]

Several subvarieties of both serpentine and amphibole are referred to in the literature as being suitable for laboratory filter aids. A large proportion of long fibers is desirable for the filtration of sugar sirups and the variety chosen should be resistant to the drastic chemical treatment described below, the purpose of which is to remove estremely fine material that may cause cloudy filtrates, and other substances that might affect the color of the solutions. Hard columnar fiber

bundles (sometimes 20 cm or more in length) should be broken to a length of 3 or 4 cm and loosened sufficiently to allow easy permeation of liquid. The asbestos fiber, in a suitable iron container such as a sand bath, is treated with a solution of sodium hydroxide, specific gravity 1.43 (40-percent NaOH), 250 ml to each 25 g. The vessel is covered and the mixture is boiled for 30 minutes with occasional stirring, no attempt being made to maintain the above concentration. The mixture is filtered by suction in a Büchner funnel without paper and washed with relays of clear tap water until substantially all alkali is removed from the filter pad. The washed asbestos, after pressing in the Büchner funnel, is transferred to a glass flask and treated with a mixture of 250 ml of hydrochloric acid, specific gravity 1.20, and 25 ml of nitric acid, specific gravity 1.42, for each 25 g of asbestos originally taken. The fiber pad is disintegrated and mixed with the acid by shaking and the mixture is heated for 30 minutes on the steam bath. The contents of the flask are then diluted with distilled water, filtered, and washed with hot distilled water until the washings give no reaction for acid or for chlorine ions. The fiber is dried at 100° to 110° C and stored in a clean container.

Asbestos for general analytical purposes has been prepared in the same manner. For the clarification of sugar solutions, three grades of long-fibered asbestos, designated consecutively according to fiber length as XXX, XX, and A [18] have been found satisfactory. Whether the asbestos is crude fiber or acid-washed, it should be subjected to the treatment described above for the removal of fines.

(b) ASBESTOS FILTERS

Several forms of filters are suitable for sirup filtration with asbestos. A 25-ml or larger Gooch crucible fitted with a disk of 200-mesh bolting silk to retain the asbestos is convenient and low-priced [40]. A good grade of filter paper (not hardened) may be substituted for the silk. Small Büchner funnels with filter paper also may be used. The size of the filter should be chosen with regard to the amount of solution to be filtered which, in turn depends upon the depth of color of the solution.

Jena glass filters [41] in the form of cylindrical funnels, 60- or 120-ml capacity with 4-cm filter element, have proved very satisfactory. These filters are designated as 11–G–1 and 11–G–2 for the 60-ml capacity, and 11–a–G–1 and 11–a–G–2 for the 120-ml capacity. The final figure designates the pore size of the filter element, No. 1 being the larger. The pore size, No. 1, is used for preliminary filtration, and the No. 2 for the final filtration.

To form the filtering pad, the asbestos in water suspension is poured into the filter, sucked down with the aspirator, and packed tightly by pressing and tapping with a flattened glass rod. The flat pad, which should be about 5 mm thick when tightly packed, is then washed a few times with water and drained by suction.

Where many samples are to be run daily, a battery of filters may be arranged as shown in figure 76. Each filter or Gooch adapter is fitted to an 8-ounce wide-mouthed bottle through a two-hole rubber stopper, the other hole being fitted with a glass tee with a two-way (Geisler) stopcock, which leads to a vacuum header, and which in

[18] Powhatan Mining Co., Woodlawn, Baltimore, Md.

turn leads to a central chamber connected with the vacuum pump or water aspirator. Each suction tube passing from the filter to the vacuum header may be closed by means of the stopcock so that the filtering process for any individual unit may be interrupted without interference with the others. The central vacuum chamber is connected with a mercury manometer or other vacuum gage.

(c) PREPARATION AND FILTRATION OF THE SOLUTION WITH ASBESTOS [42]

A generous supply of solution should be available, the amount to be taken depending upon the depth of color. For darker products, 100 g of solution may be sufficient, whereas 200 g or more may be necessary for white sugars. The stability of transparency is, in large part, dependent upon high density. It is therefore considered necessary that the dry-substance concentration of the solution be not lower than 60 Brix, which is compatible with reasonably rapid filtration. Time is saved by dissolving and diluting on a weight basis. The required weights of sample and water are calculated as follows:

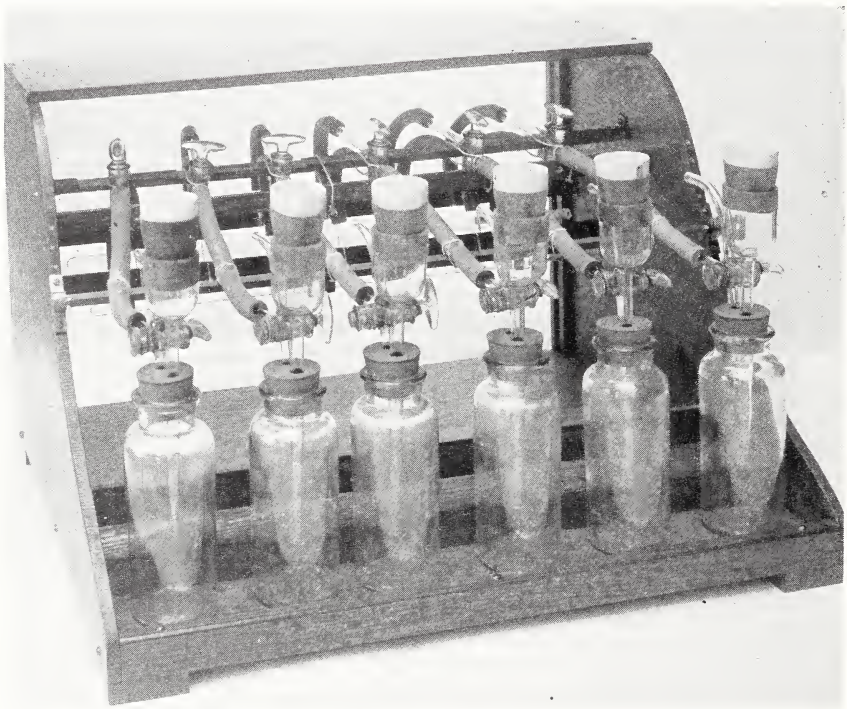

FIGURE 76.—*Peters and Phelps filter battery.*

$$\frac{\text{g solution required} \times \text{Brix of solution}}{\text{Brix of sample}} = \text{g sample to be taken.}$$

Then

$$\text{g water to be added} = \text{g solution} - \text{g sample.}$$

For nearly dry products of relatively high purity, such as 96 test raw sugars, a sufficiently close approximation results if polarization is substituted for Brix.

The calculated amount of sample to provide a 60-Brix solution is weighed into a tared flask on a rough balance and weights equivalent to the required water are added to the pan. A small amount of hot distilled water is added and the flask is placed in a water bath heated to 50° C and shaken to promote rapid solution. Hot water is added to the flask a little at a time until the sample is dissolved. The flask is dried on the outside and returned to the balance pan where dilution to the required weight may be completed. Purified dry asbestos is added to the solution in amount depending upon the quantity and character of the suspended matter present. Usually 0.5 g will suffice, but when slimy material is present and the solution is refractory in filtration, 1 to 2 g should be used. The flask is loosely stoppered and shaken gently at first until the warm air is expelled. The stopper is then tightened and the flask is shaken vigorously to mix the contents thoroughly and to permit the asbestos fibers and the suspended matter to become entangled. The flask is returned to the bath and the solution is allowed to warm for a short time.

Although it is possible to obtain a satisfactory filtrate with a single filtration, particularly in the case of easy filtering solutions, it is customary to filter twice. Two filters are therefore prepared as directed in section (b), p. 325. The first, or preliminary filter, immediately before filtration, is warmed by washing with a small amount of hot distilled water, which is aspirated from the asbestos pad as thoroughly as possible. The warm solution is then added and a few milliliters filtered to displace the water remaining in the pad when the suction is closed off and a clean dry receiver is substituted. When the filtration is resumed the remainder of the solution, or as much as the filter will hold, is added. The pad is to be kept covered with solution during the filtration, at the end of which the suction is stopped before the pad becomes uncovered. The receiver is detached and returned to the bath for further warming while the second filter is being rinsed with hot water and drained. The second filtration is performed exactly as the first but no asbestos is added to the first filtrate. The main portion of the filtrate is collected in a clean receiver. This filtrate is cooled and adhering condensed water is wiped from the neck of the bottle which is then closed with a clean, dry stopper and shaken to mix the contents throughly. The refractometric Brix of the optical filtrate is determined and c (g dry substance per 1 ml) is obtained by reference to table 114, p. 632). The solution, if not too dark, is now ready for photometric observation.

(d) PREPARATION OF DIATOMACEOUS EARTH AND FILTRATION

Diatomaceous earth, also known as infusorial earth or kieselguhr, on account of its availability and ease of application, is preferred in factory laboratories for the clarification of sugar solutions for colorimetry. As noted by Balch [57], variable quantities of earth must be used to obtain satisfactory clarification, depending upon the nature and amount of suspended matter present as applying to different grades of sugar products. Zerban and Sattler [58] found that the same statement applies to products of a single grade (raw sugar), and that there is a gradual falling off in $-\log \mathbf{t}$ in some cases with increasing quantities of earth used, and that more earth than the quantities tested (5 g to 50 ml of 60 Brix) would have to be used to reach a limiting effect.

Experience at this Bureau [42] and as reported elsewhere [59] has led to the belief that diatomaceous earth has a distinct decolorizing effect upon sugar solutions beyond the removal of visible turbidity, depending upon the quantity of earth used and the number of filtrations.

On the basis of time consumed in obtaining satisfactory filtrates, a comparison of clarification with asbestos or with diatomaceous earth probably leaves little to choose, much depending upon the development of technique. For technical purposes, where an error of a few percent is of little consequence, and where the employment of earth is more convenient, its use is recommended, particularly for the filtration of thin juices.

Diatomaceous earth should be treated for the removal of interfering substances, as described below.

Methods for purifying diatomaceous earth by means of dilute hydrochloric acid have been described by Zerban and Sattler [58] and by Honig [60]. In the method employed at this Bureau, 100 g of earth in an Erlenmeyer flask is treated with 400 ml of strong hydrochloric acid and 40 ml of strong nitric acid. The contents of the flask are mixed and heated for 30 minutes on the steam bath. The mixture is then diluted with 2 liters of cold water, and the earth is allowed to settle for a few minutes when the liquid is decanted. The earth is then filtered with suction in a Büchner funnel and washed with relays of dilute hydrochloric acid (20-percent concentrated acid by volume) until the filtrate shows absence of iron, then with distilled water for removal of hydrochloric acid. The product is dried at 110° C.

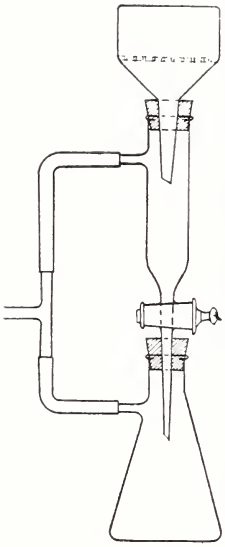

FIGURE 77.—*Filter apparatus of Zerban and Sattler.*

Zerban and Sattler boil 75 g of earth with a mixture of 100 ml of concentrated hydrochloric acid and 900 ml of distilled water and filter hot, then wash thoroughly with hot water. This treatment is repeated three times, and the material is dried and ignited in a muffle furnace.

For the clarification of solutions of washed raw or better-grade sugars, 100 to 200 ml of the 60-Brix solution is treated in a suitable flask, with 2 percent of the purified earth based on the weight of solids. For badly contaminated products, more earth must be used. The flask is closed with a rubber stopper and vigorously shaken, and the mixture is filtered through a double layer of a good grade of paper, 5.5 cm in diameter, in a Büchner funnel. The paper should first be washed with a little water. When the filtrate has become clear, a clean, dry receiver is substituted and the filtration is completed. As suggested by Balch [57], receivers may be changed without the necessity of breaking the vacuum if the Büchner funnel is connected to a fractional distillation receiver designed for distillation under reduced pressure. To complete the filtration without breaking the vacuum, Zerban and Sattler use the apparatus shown in figure 77.

Balch states that the more resistant the suspended material is to filtration, the more earth must be used which may amount to as much

as 10 percent on solids, and for cane juices or lime-defecated juices the maximum will undoubtedly be necessary.

Honig [60] treats 200 ml of 55-Brix solution of sugar in a 300-ml Erlenmeyer flask with 2 g of prepared Hyflo Supercel. After mixing, the solution is filtered on a Büchner funnel through a hardened paper that has been slightly moistened beforehand. The suction is turned on and the entire amount of the mixture is added to the filter. The filtrate is refiltered five times through the original layer of filter-aid, finally being collected in a clean receiver.

7. DILUTION OF COLOR [40, 42]

A dilution of color is necessary when the saccharine product is too dark to permit good photometric readings, particularly when observations are to be made in the blue portion of the spectrum. Dilution with water alone causes separation of colloids which produce turbidity. The dilution may be accomplished, however, by the addition of a concentrated, highly decolorized sugar solution to the turbid dark solution, or by mixing a known weight of white sugar with the sample, and diluting.

To prepare the diluent sirup, a 60–Brix solution of the best obtainable grade of white sugar is heated in a bath to 90° C. Decolorizing carbon equivalent to 2 percent of the weight of sugar solids is added and the mixture is warmed and shaken during 15 minutes. Prepared kieselguhr (see section 6 (d), p. 327) 5 percent on solids, is added and mixed with the solution, which is then filtered through paper in a large Büchner funnel, cloudy first-runnings being returned to the filter. The solution is refiltered through an asbestos pad. The color remaining in the sirup after a single carbon treatment depends upon the color of the original sugar. Usually there is detectable light absorption in the blue part of the spectrum, but this should be so slight as to be negligible in the final results. It is possible, by repeated carbon treatment, to prepare solutions that absorb no mercury blue-violet in a 20-cm thickness of liquid column.

The dilution of color with sirup may be carried out on a volume or a weight basis. The volume basis is more rapid, but the weight basis is more precise, since deduction may be made for any absorption by the diluent. When dry white sugar is used, the dilution is necessarily on a weight basis. In the following description of the procedure the same colored product and the same diluent sugar were used, the latter being a specimen sold as pure sucrose. In procedures (a) and (b) the diluent solution was not treated with decolorizing carbon but was filtered through asbestos.

(a) VOLUME BASIS

The two solutions, which should be at the same temperature (20° to 25° C), are pipetted into a flask, the pipettes used being graduated to contain a definite volume. Both pipettes are rinsed with the solution in the flask, after it is mixed, in order that the adhering solution may be of the same concentration as that in the flask. The mixture is filtered through asbestos at room temperature, and the transmittancy is measured with the photometer. The following example illustrates the calculations.

Colored solution, refractometric Brix	60. 3
Colored solution, c, from table 114	0. 7768 g/ml.
Colored solution, volume taken	20. 0 ml.
Diluent solution, volume taken	100. 0 ml.

The mixture then contains one-sixth of its volume of colored solution, and c, the colored dry substance of the mixture, therefore beomes $0.7768/6=0.1295$.

Thickness of absorption cell, b,$=2.0$ cm.

$\mathbf{T}$ at $\lambda 436$ mμ by photometer$=0.34$.

$-\text{Log } \mathbf{T}_{\lambda=436}$ from table 129$=0.4685$.

Since $-\log \mathbf{t}=1/cb\times(-\log \mathbf{T})$,

$$-\text{Log } \mathbf{t}=\frac{1}{0.1295\times 2}\times 0.4685=1.8089.$$

(b) WEIGHT BASIS

This procedure is longer than (a) but is capable of yielding more precise results, since a correction is introduced for any absorption by the diluent sirup. It is therefore necessary to know the dry-substance content of both colored solution and diluent and $-\log \mathbf{t}$ of the diluent at the wave lengths selected. The same values are then determined for the mixture and the corrections are applied.

A portion of the colored solution is weighed in a tared flask or beaker, and the diluent in the desired amount is added and the whole reweighed and mixed, the weight of added diluent being found by difference. The mixture is warmed to 60° C, filtered with asbestos, cooled, and the refractometric Brix is determined. The transmittancy of the mixture in appropriate cells is then read at the selected wave lengths with the photometer. The manner of applying the corrections is illustrated by the following example, in which the values for the diluent sirup are first determined.

Example.—In the diluent sirup Brix$=60.9$, corresponding to $c=0.7867$ (table 114, p. 632). Cell length, $b=20$ cm. $\mathbf{T}_{\lambda=560}=0.887$, $\mathbf{T}_{\lambda=436}=0.699$. From table 129 then we obtain $-\log \mathbf{T}_{\lambda=560}=0.0521$, $-\log \mathbf{T}_{\lambda=436}=0.1555$.

Substituting in the Lambert-Beer equation, we have

$$-\log \mathbf{t}_{\lambda=560}=\frac{1}{0.7867\times 20}\times 0.0521=0.0033.$$

$$-\log \mathbf{t}_{\lambda=436}=\frac{1}{0.7867\times 20}\times 0.1555=0.0099.$$

In the colored solution, Brix$=60.3$ corresponding to $c=0.7768$.

Weight of colored solution taken	12. 415 g.
Weight of mixture after adding diluent	73. 480 g.
Difference=weight of diluent	61. 065 g.

Weight of dry substance in colored solution$=60.3$ percent of $12.415=7.4862$ g.
Weight of dry substance in diluent$=60.9$ percent of $61.065=37.1886$ g.
Weight of dry substance in the mixture$=44.6748$ g.

Percentage of colored dry substance$=\dfrac{7.4862}{44.6748}=16.75$

After filtration and cooling, the refractometric Brix of the final filtrate was 62.0, or $c=0.8049$. Assuming that the proportions of colored and diluent dry substance do not change upon concentration, we have in the final filtrate $c=16.75$ percent of $0.8049=0.1348$ and diluent dry substance, $c_D=0.8049-0.1348=0.6701$. The photometric readings of this mixture in a 2-cm cell were $\mathbf{T}_{\lambda=560}=0.72$ and $\mathbf{T}_{\lambda=436}=0.33$. Corresponding to $-\log \mathbf{T}_{\lambda=560}=0.1427$ and $-\log \mathbf{T}_{\lambda=436}=0.4815$.

Substituting in the Lambert-Beer equation, we have

$$-\log \mathbf{t}_{\lambda=560}=\frac{1}{0.1348\times 2}\times 0.1427=0.5293,$$

$$-\log \mathbf{t}_{\lambda=436}=\frac{1}{0.1348\times 2}\times 0.4815=1.7859.$$

In the mixture it is obvious that the absorbancy, which we shall call $-\log \mathbf{T}_M$, is made up of two parts, the $-\log \mathbf{T}$ of the colored solution and the $-\log \mathbf{T}_D$ of the diluent solution, that is,

$$\text{(a).}\qquad -\log \mathbf{T}=(-\log \mathbf{T}_M)-(-\log \mathbf{T}_D).$$

The value of $-\log \mathbf{T}_D$ may be calculated by the Lambert-Beer law if we know the concentration, c_D, of the diluent dry substance in the mixed solution and its specific absorptive index, $-\log \mathbf{t}_D$, for each wave length as follows:

$$\text{(b).}\qquad -\log \mathbf{T}_D=c_D b(-\log \mathbf{t}_D).$$

In the mixture, we have already found by difference that $c_D=0.6701$, and $-\log \mathbf{t}_D$, as already determined in the diluent to be 0.0033 for $\lambda=560$, and 0.0099 for $\lambda=436$. Substituting these values in (b), we have

For $\lambda=560$, $-\log \mathbf{T}_D=0.6701\times 2\times 0.0033=0.0044$.

For $\lambda=436$, $-\log \mathbf{T}_D=0.6701\times 2\times 0.0099=0.0133$.

Substituting these values of $-\log \mathbf{T}_D$ in (a), we have

For $\lambda=560$, $-\log \mathbf{T}=0.1427-0.0044=0.1383$

For $\lambda=436$, $-\log \mathbf{T}=0.4815-0.0133=0.4682$

These are now the corrected values for $-\log \mathbf{T}$ in the mixture and we recalculate the values of $-\log \mathbf{t}$

$$-\log \mathbf{t}_{\lambda=560}=\frac{1}{0.1349\times 2}\times 0.1383=0.5125.$$

$$-\log \mathbf{t}_{\lambda=436}=\frac{1}{0.1349\times 2}\times 0.4682=1.7351.$$

The differences from the uncorrected values for the mixture in procedure (b) are found to be 3.28 percent for $\lambda=560$ and 2.93 percent for $\lambda=436$. In procedure (a) the difference is 4.25 percent, the divisor in each case being the corrected value.

(c) DILUTION WITH SOLID SUGAR

A high-grade, refined, white sugar selected for absence of color may be used to advantage for color dilution. A large quantity, when properly stored, may be kept on hand over a long period without danger of serious change in color. The absorption data may be determined once for all and applied as a correction when necessary. The preparation of a diluent sirup is thus avoided.

A portion of the white sugar is weighed in a sugar dish or other suitable vessel. To this is added the colored product (with known Brix) in quantity to produce the desired color in the mixture, and the weights of each are recorded. The mixture is transferred with a small quantity of hot water to a tared flask, the dilution to 60 Brix is completed and the warm solution filtered through asbestos (section 6 (c), p. 326). After cooling the solution the refractometric Brix is determined and the transparent solution is measured photometrically.

The weight of water required for dilution to 60 Brix may be calculated if the total dry substance of the mixture is known. For example, if 5 g of 80-Brix molasses is added to 60 g of white sugar (assuming 100 percent of dry substance in the latter), then the weight of total dry substance in the mixture is 64 g. The weight of a 60-Brix solution of the mixture is then $100\times 64/60=106.7$ g, and the water required is $106.7-64=42.7$ g.

To find the colored dry substance in the mixture after the asbestos filtration the directions as given in procedure (b) are followed. In the present case, for example, as we have seen, 5 g of 80-Brix molasses contains 4 g of dry substance. Adding this to the 60 g of dry substance of the white sugar, we have 64 g of total dry substance in the mixture. Of this, 4/64, or 6.25 percent, is colored dry substance,

Assuming that the refractometric Brix of the cooled asbestos filtrate was found to be 61.2, ocrresponding to 0.7917 g of dry substance per 1 ml, then the colored dry substance is 6.25 percent of 0.7917, or 0.0495 g per 1 ml, the value to be taken for c in the Beer's-law equation. If correction for absorption of the white sugar is necessary, the calculations are made in exactly the same manner as in procedure (b).

(d) CALCULATION OF BRIX

In case the Brix (percentage of dry substance by weight) of a heavily colored product is unknown, the original Brix may be calculated from data obtainable in procedure (b) or (c) and the results are as nearly correct as those obtained by methods usually applied to low-grade products. To obtain the Brix of the colored sample the weight of dry substance in the diluent is subtracted from the weight of dry substance in the mixture (determined from the weight of the mixture and its Brix before filtering). The remainder is divided by the weight of the colored sample and the quotient is multiplied by 100. Or, expressed as a formula:

$$\text{Brix sample} = 100 \times \frac{(\text{g mxt.} \times \text{Brix \% mxt.}) - (\text{g diluent} \times \text{Brix \% diluent})}{\text{g of sample}}.$$

For example, if the Brix of the colored sample in procedure (b) were unknown and if the refractometric Brix of the turbid mixture as found immediately after mixing was 60.8, then

$$\text{Brix of sample} = 100 \times \frac{(73.48 \times 0.608) - (61.065 \times 0.609)}{12.415} = 60.31.$$

When procedure (c) is used, the weight of diluent dry substance is represented by the weight of white sugar taken, and the mixture may be dissolved and diluted by warming to 50° C in a bath, but, as noted before, in order to determine the unknown Brix of the colored product, the solution must be cooled and thoroughly mixed, then weighed, and its refractometer reading made before filtering. These operations are carried out with the substances in the original tared flask.

8. SUMMARY OF THE PROCEDURE

When dilution of color is unnecessary:

1. Make up a 60-Brix solution of the sugar product.
2. Filter with asbestos as described.
3. Determine the refractometric Brix, and from table 114, p. 632, find the corresponding grams of dry substance per milliliter ($=c$), or calculate c from refractometric Brix and true density thus,

$$c = \frac{\text{Brix} \times \text{true density}}{100}.$$

4. Fill a parallel-sided cell of suitable thickness with the solution, and a duplicate cell with the solvent (water) to be placed in the comparison beam. Read the transmittancy on a spectrophotometer, a simplified spectrophotometer, or other comparator capable of measuring transmittancy for monochromatic light.

5. Record
   (a) c=grams of dry substance per milliliter of final filtrate.
   (b) b=thickness of the absorption cell used.
   (c) **T** or $-\log$ **T** for each wave length as read.

6. Reduce the readings obtained to unit basis as regards concentration and thickness by calculating specific absorptive index, $-\log$ **t** from the equation, $-\log \mathbf{t}=1/cb\ (-\log \mathbf{T})$.

When color is diluted record also:

7. For volumetric method, procedure (a):
   (a) Grams of dry substance per milliliter ($=c$) of turbid solution.
   (b) Volume of turbid solution.
   (c) Volume of diluent solution.
   (d) Grams of colored dry substance per milliliter in mixture.

8. For gravimetric method, procedure (b), for correction of $-\log$ **t**:
   (a) Refractometric Brix of diluent sirup.
   (b) Weight of diluent sirup or solid sugar.
   (c) Specific absorptive index, $-\log \mathbf{t}_D$ of diluent.
   (d) Refractometric Brix of colored sugar product.
   (e) Weight of sugar product taken.

After filtration with asbestos, record:

   (f) Refractometric Brix of final filtrate.

For qualitative and quantitative investigation of sugar color, readings are made at wave-length intervals of 10 or 20 mμ over that part of the spectrum included between 420 and 700 mμ. For routine technical purposes a reading at the single wave length 560 mμ is sufficient, which, with the use of the filters designated for the purpose, may be done directly with a simple instrument or by calculation from readings at λ546.1 and λ578 mμ of the mercury arc (see paragraph 10, below).

9. For some purposes it is convenient to reduce $-\log$ **t** at 560 mμ to n units of coloring matter (equivalent to n sugar color degrees). This is to be done by dividing $-\log$ **t** by the absorption unit, $-\log$ **t**, of the standard at the same wave length. This value ($-\log \mathbf{t}_1$) for the provisional standard adopted is 0.00485 at λ560 mμ for all types of coloring matter usually occurring in sugar products. It is now known as the Peters and Phelps color unit. One absorption unit at 560 mμ is equivalent to one unit of coloring matter which evokes a color sensation of one color degree. The value, n, absorption units, represents the sum total effect of absorption at all wave lengths. It is therefore a measure of n units of coloring matter in 1 g of sugar-dry substance and may be used as the final value to be regarded as characteristic of the sample measured.

In all cases additional measurements at other wave lengths than 560 mμ, especially the shorter wave lengths (for example, the Hg lines 546 mμ and 436 mμ), may be made to yield valuable information as to changes taking place in various processes of manufacture, especially when studied as absorption ratios.

10. When the mercury arc is used as light source, a reading at 560 mμ may be obtained by a process of interpolation between readings at 546.1 and 578 mμ or by applying a correction factor as follows: Deduct 48 percent of the difference between $-\log$ **t** at λ546.1 and λ578 from $-\log$ **t** at λ546.1; the result is $-\log$ **t** at λ560.

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9. COLOR STANDARDS FOR SOLID SUGARS

Reference has already been made in this chapter to the measurement of reflectance from a smoothed surface of solid sugar, using certain of the photometric instruments described in previous sections. In some countries duty on imported sugar is charged according to color as well as to polarization, i. e., a higher duty is paid on a sugar lighter than a certain standard than on one that is darker. As a basis for color comparison, the well-known Dutch Standards are used.

The Dutch color standards consist of a series of samples of crystalline sugars of approximately equal gradations of color ranging from No. 7, which is very dark, to No. 25, which is almost white. Number 16 Dutch Standard is the technical color distinction in some countries between refined and raw sugars. The color grade of any given sample is determined by comparison with the standard series. The standards contained in sealed bottles are prepared for the sugar trade by a firm in Holland. They should be renewed once a year because of the tendency of the colors to change.

Color standards for soft sugars were prepared from ground glass by Wills [61]. The glass specimens (designated as colorless, light brown, dark amber, and uranium yellow) after grinding, were mixed in varying proportions and graded to give gradually increasing color. In all, 26 samples were formed. Later, the reflectance of these samples was measured with a Keuffel & Esser color analyzer and any necessary adjustments were made.

Raw-sugar color standards were prepared by Spengler and von Heyden [62] by coating white sugar crystals with yellow ochre (dark), cadmium yellow, and Norit, in various proportions. The pigments were first thoroughly mixed with a 67-percent solution of white sugar. The crystalline sugar, after mixing with the pigment suspension, was centrifuged and the coated sugar first air-dried, then heated in the oven for ½ hour at 70° to 80° C. The cooled samples were then placed in containers having Cellophane windows.

10. DECOLORIZING EFFICIENCY OF CARBONS

(a) FINELY DIVIDED CARBONS

(1) Determination of Moisture.—Decolorizing carbons are capable of retaining several percent of moisture, depending upon humidity conditions, and the main sample should therefore be stored in a tightly stoppered bottle. In order to maintain a uniform basis of comparison among different lots of carbon, it is necessary that the results of decolorizing tests be calculated to moisture-free material.

Approximately 2 g of carbon is weighed in a large, tared weighing bottle provided with a stopper, and heated 12 hours or overnight in an oven maintained at 150° C. At the end of the heating period, the bottles are stoppered and transferred to a desiccator while still warm. The bottle with contents is weighed after cooling. The loss of weight of the sample is calculated to percentage of moisture.

(2) Decolorizing Efficiency.—The removal of sugar color from solutions by carbon has been shown by several investigators [43, 44, 47, 48, 49, 50] to follow the general adsorption equation, or isotherm, expressed by Freundlich [51, 52] as follows:

$$\frac{x}{m}=kC^{1/n},$$

where x is the amount of color removed by m grams of carbon, C is the amount of color left in the treated solution at equilibrium, and k and $1/n$ are constants, which for any given solution are characteristic of the carbon.

Writing the Freundlich equation in logarithmic form, we have

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C,$$

the equation of a straight line. If log x/m as ordinates is plotted against log C as abscissas on rectangular coordinate paper, log k is determined as the value of the ordinate, where $C=1$ (or 100, where percentage of decolorization is used), while $1/n$ represents the slope of the isotherm. The factor $1/n$ is equal to the tangent of the angle formed by the isotherm with the log C axis. The values for C and x are best expressed in terms of percentage of the color of the original solution before treatment. This in turn may be in terms of $-\log$ **t**, $-\log$ **T**, or any of the usual color units. The value of m may be expressed as grams of carbon, or as percentage carbon on sugar-dry substance.

The extent of decolorization of sugar solutions by a carbon is dependent upon several factors, among which are time of contact, temperature, concentration, pH, and nature of the sugar product [49]. In comparing carbons, therefore, it is necessary that these conditions be kept uniform. Also, it is generally agreed that the test material should be similar to that to be treated on the large scale.

As test materials, diluted molasses or high-density solutions of raw sugar are most frequently used in the sugar industry. The former permits the more rapid work, whereas the latter is capable of affording more accurate results which may be made directly applicable to large-scale practice. Washed raw sugar, dried at the ordinary temperature and well mixed, may be stored in large quantity and is recommended for the isotherm test.

Using washed raw sugar, 500 g is dissolved in 350 ml of water at 90° C, and 20 g of kieselguhr (or more if necessary) is added and mixed. The mixture is filtered in a large Büchner funnel fitted with two layers of paper (Whatman No. 42 or equivalent) which has been moistened and the excess water removed by suction. Small quantities of the mixture are filtered at first, and, if the filtrate appears to be perfectly clear, the main portion is filtered. In case of cloudy first-runnings, the mixture may be added little by little until a sufficient amount of kieselguhr has become deposited to give a clear filtrate. The funnel is then transferred to a clean receiver and the filtration completed, including the cloudy first-runnings. The filtrates may be improved by a second filtration, through asbestos, using a 120-ml Jena No. 1 funnel. The solution is cooled, thoroughly mixed, and the Brix is determined with the refractometer.

For convenience, such amounts of the solution are taken for carbon treatment as to contain 100 g of dry substance each (found by dividing 100 by the Brix as a decimal, thus $100/0.60=166.67$ g). This amount is weighed to within 0.1 g in each of four tared 250-ml Erlenmeyer flasks. These are placed in a bath held at 90° C and allowed to warm. In the meantime, 4 portions of the carbon under test are weighed out (to 1 mg) equivalent to 0.5, 0.7, 1.0, and 1.5 g (or percent

on sugar solids), moisture-free basis, each weighed portion being placed in a scoop or trough made by bending a 3- by 4-inch sheet of thin aluminum or brass. It may be necessary to vary the quantities of carbon from those given, depending upon the color of the solution and the decolorizing ability of the carbon. A weighed portion of the carbon is transferred to each flask, which is shaken continuously in the heating bath for 15 minutes. The carbon is best removed by filtration on an asbestos pad, using a Jena No. 1 filter. For paper filtration, approximately 1 g of kieselguhr is mixed with the contents of each flask, which is filtered by suction through a double layer of Whatman No. 42 paper, 7.5 cm in diameter, in a Büchner funnel. A battery of four filters with clean, dry receivers may be arranged and an extra receiver used for starting the filtration of each solution, in turn. When the filtrate becomes perfectly clear, the filter is placed in its receiver and the filtration completed. The decolorized solutions are cooled and thoroughly mixed, the refractometer Brix of each is determined, and the solutions, including the original undecolorized liquor, are evaluated photometrically, preferably at 560 mμ, the thickness, b, of the light-absorbing layer being governed by the color of the solution. From the Brix, layer thickness, and photometer readings (giving c, b, and **T** for each solution), $-\log$ **t** is calculated as already described. These values of $-\log$ **t,** without conversion to color units, are used for computing the values for plotting the isotherm.

Table 40 illustrates the manner of computing the isotherm data. The values of C are found by ($-\log$ **t** decol./$-\log$ **t** orig.)$\times$100 to give a whole number and $x=100-C$. The values of m as given may be called the percentage of carbon on saccharine dry substance.

TABLE 40.—*Computation of data for the isotherm in figures 78 and 79*

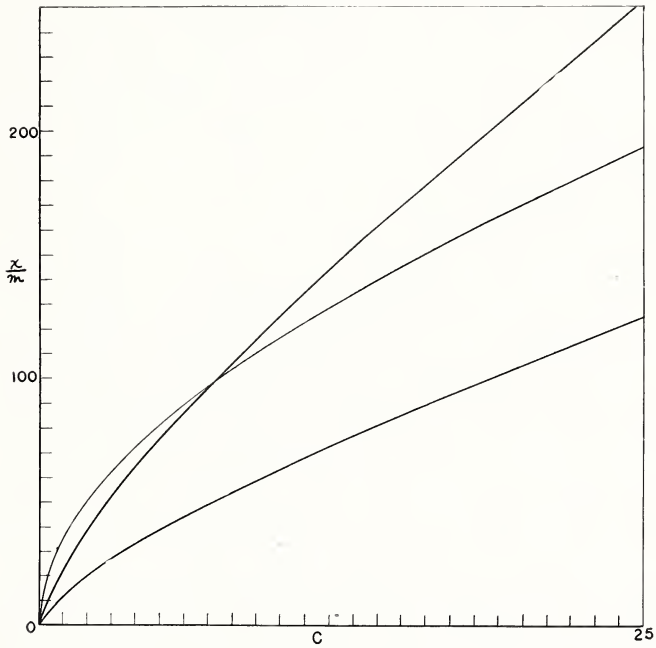
m=grams of carbon	$-\log t$, 560 μ	C	$x=100-C$	x/m
0.0	0.2090	100.0	-------	-------
.5	.0316	15.1	84.9	169.8
.7	.0211	10.1	89.9	128.4
1.0	.0136	6.5	93.5	93.5
1.5	.0082	3.9	96.1	64.1

The values of log x/m may now be plotted against log C as rectangular coordinates, or as recommended by Sanders [45], x/m and C are plotted on double logarithmic paper, as shown in figure 79, the data being those of table 40.

Diluted molasses is preferred by many as a material for the decolorization test, since the solutions are easily filtered without suction. Diluted molasses is unstable in color, and stock solutions should therefore be prepared at least daily. This stock solution should not be too dark for ease of color determination or so light that it is too easily decolorized.

The procedure as outlined by Sanders [44] is as follows: Equal volumes (150 ml) of the molasses are pipetted into five 250-ml Erlenmeyer flasks. These are placed in a water bath and heated to 90° C. On each of five strips of white glazed paper 1 g of Filter-Cel is placed. Four portions of carbon are weighed, using, for instance, 0.1, 0.2,

0.4, and 0.7 g weighed to the nearest mg, allowance being made for the moisture content of the carbon. Each weight of carbon is placed on the Filter-Cel on each of the strips. The Filter-Cel alone is added to one of the flasks and the mixture of Filter-Cel and carbon to the other four. The heating is continued during 10 minutes after the addition, the flasks being shaken continuously. The flasks are removed from the bath and their contents filtered through paper on separate 60° funnels. Cloudy first-runnings are discarded or returned to the filter, only brilliantly clean filtrates being accepted for colorimetry. After cooling, the filtrates are measured photometrically, preferably at wave length 560 mμ. Concentration of dry substance is not taken into account in this procedure. Thicknesses



ADSORPTION ISOTHERMS

FIGURE 78.—*Adsorption isotherms of three decolorizing carbons.*
C Concentration of coloring matter remaining in solution plotted against x/m, where x is the amount of coloring matter removed by m grams of carbon.

(*d*) are reduced to 1 cm by dividing —log **T** as found or calculated from the photometer reading, by the length in centimeters of the cell used. If Meade-Harris color units are used, the number of units found, corresponding to the photometer scale reading, are divided by the cell thickness in centimeters.

Depending upon the system used, either —log **T** or the Meade-Harris color unit of the untreated molasses solution is taken as the basis for calculating the percentage of original color remaining, (C), and the percentage of color removed, (x). Knowing m from the weight of carbon, x/m is computed, and the results are plotted on double logarithmic paper, as recommended above.

Sanders [45, 46] has applied the adsorption isotherm to calculate the amount of carbon to be used to reach a desired degree of decolorization and also to compute the decolorization and the carbon required in countercurrent work.

Although one may read the values of x/m and C from the isotherm plot and may calculate m from the relation $x+C=1$ (if color is expressed as a fraction), this computation is done more easily by reference to the nomograph shown in figure 80.

This nomograph solves the equation $Y/M=K(1-Y)^{1/n}$. This is the same as $x/m=kC^{1/n}$, where the color is a fraction of the original

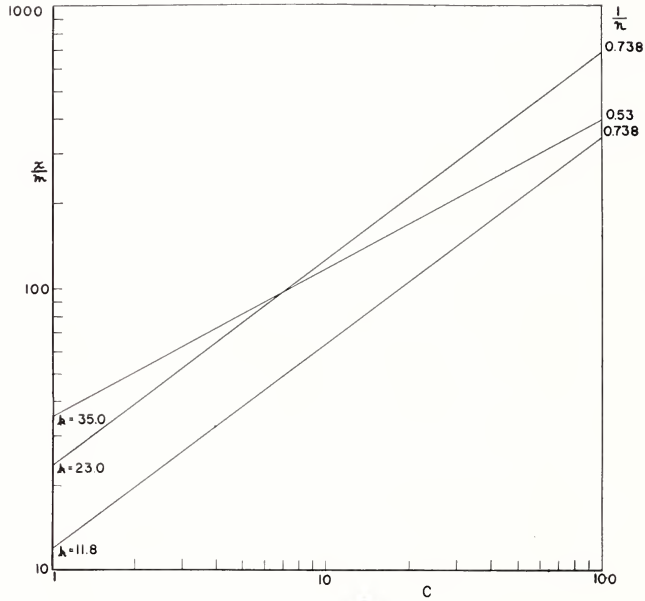


FIGURE 79.—*Adsorption isotherms of the same three decolorizing carbons shown in figure 78 (plotted on a logarithmic scale).*

k, A constant (value of ordinate, where log $C=1$); $1/n$, a constant (slope of the isotherm or tangent of the angle formed by the isotherm with the log C axis).

color, $x=y$ and $C=1-y$. To exemplify the use of the chart, let us suppose that the values for K and $1/n$ were found to be 3 and 0.610, respectively, and that it is desired to know how much carbon is necessary to remove 70 percent of the color. On figure 80 draw a straight line from $1/n=0.61$ to $Y=70$, and extend this line to the MK axis. The line extended cuts this axis at 1.45. Since $K=3$, then $M=1.45/3=0.483$ g (or pounds) of carbon per unit volume of solution. In describing a carbon in terms of K and $1/n$, it is necessary to adopt standards of mass and volume of carbon and solution, respectively.

(b) GRANULAR BONE BLACK

The sample of bone black may be pulverized and tested for decolorizing efficiency in the same manner described for the char powders. However, since the two kinds of carbon differ so greatly in grain size

and in other properties, and since the mode of application in practice is different, the refinery chemist prefers to use a method that is more nearly representative of practical working conditions.

Experimental methods of evaluating bone chars are described by Wayne [53] and by Knowles [54], both of whom apply the char to the sugar solution on a weight basis. Blowski and Bon [49] apply the carbon on a volume basis. They place 170 ml of bone char in a 500-ml flask containing 10 ml of Filter-Cel and add 200 ml of a 47.5-Brix solution of crystallizer remelt sugar. The mixture is shaken and digested 3 hours on the water bath with 30-second periods of shaking every half hour. The mixture is decanted into paper filters and allowed to filter overnight. A blank and an arbitrary standard

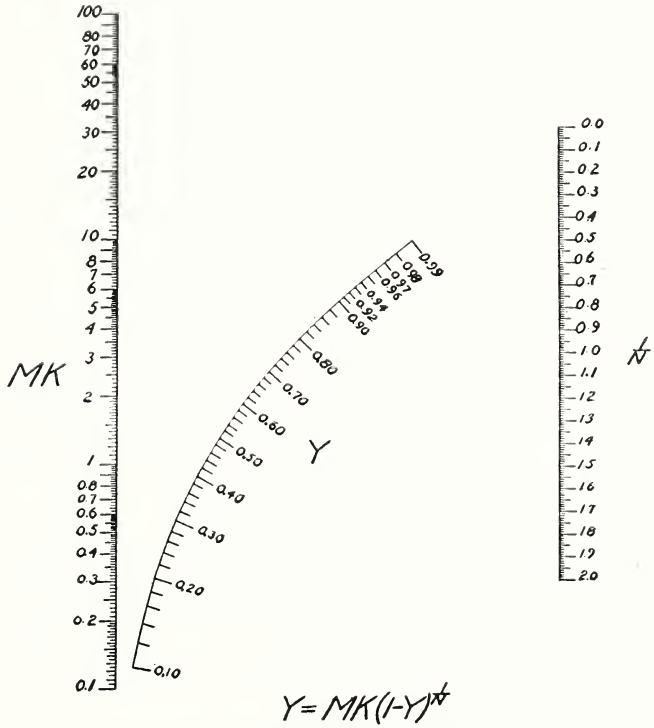


FIGURE 80.—*Nomograph for calculating, from the isotherms, the amount of carbon required to reach a desired degree of decolorization.*

char are submitted to the test in parallel. The color remaining in each filtrate is determined and the decolorizing efficiencies are compared with that of the arbitrary standard.

In the Spencer-Meade handbook [55] is described a procedure in which the weighed bone black is placed in cylindrical copper funnels, diameter 4 inches and height 15 inches, each provided with an outlet pipe and cock at the bottom. The char rests on a perforated copper plate covered with cloth. The funnels are placed in a water bath, provided with suitable openings for the outlet cocks and are filled to within a few inches of the top with the chars to be compared, the weight of char in each filter being the same.

A 55-Brix solution of a molasses sugar clarified by filtration with kieselguhr is used for the test. The liquor is heated to 165° F (73.9° C) and equal portions are added, little by little, to avoid air pockets. After the char is covered, the remainder of the liquor is poured into the filter. The temperature of the water bath is maintained at 160° to 170° F (71.2° to 77.2° C) for several hours, and the liquor is then drawn off through the outlet cocks. The color of the filtrates and of the untreated liquors are compared.

In this procedure it may be necessary to clarify the char filtrates, if char particles are present, by further filtration with kieselguhr, and changes in the concentration of dry substance may be detected by means of the refractometer.

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XX. MEASUREMENT OF TURBIDITY

1. METHOD OF BALCH

The method proposed by Balch [1] for the measurement of turbidity in sugar products is based upon the principle of measuring the transmittancy of light through the turbid solution, matched against a portion of the same solution from which turbidity-causing material has been removed by filtration. The color of the turbid solution is thus compensated by the filtered portion.

The procedure described here is taken mainly from Balch's article. The instrument used was a Keuffel & Esser spectrophotometer, all measurements being made at wave length 560 mμ.

Juices and many factory sirups may be filtered without dilution. In the case of high-density or solid products, a density greater than 60 percent of solids is not recommended. A 100- to 200-g portion of the turbid sugar solution to be tested is filtered with 2 to 10 percent of kieselguhr (based on sugar solids). The quantity of filter aid to be used depends upon the quantity and character of the suspended material affecting filtration. After mixing the kieselguhr very thoroughly with the sample, it is filtered at room temperature under diminished pressure through paper in a Büchner funnel which may be attached to a fractional distillation receiver whereby containers may be changed without breaking the vacuum. The filter apparatus of Zerban and Sattler (fig. 77, p. 328) serves the same purpose. After 25 to 50 ml of the solution has filtered, the remainder is received in a clean container. This last portion should appear brilliantly clear by transmitted light.

The turbid untreated portion of the solution is freed from coarse suspended material by straining through 200-mesh bolting silk, and freed from air bubbles by subjecting the sample to vacuum, con-

veniently in the fractional distillation receiver at the time of filtration. The percentage of solids is determined with a refractometer.

In one of a matched pair of absorption cells is placed a portion of the clarified solution and in the other a portion of the strained and bubble-free turbid solution. The choice of thickness of the absorbing layer to be chosen depends upon the depth of color and turbidity of the solutions. For white sugars, cells 10 cm long or longer are needed, while for raw sugars a thickness of 1 cm or less is sufficient. The cells are mounted on the spectrophotometer and the transmittancy readings are taken in the usual manner. The accepted transmittancy value (the average of a number of readings) is then reduced by means of the Lambert-Beer formula to the specific absorptive index,

$$-\log \mathbf{t}=\frac{1}{cb}(-\log \mathbf{T}).$$

Since the color of the turbid solution is compensated by that of the clarified solution, $-\log \mathbf{t}$ is taken to represent the turbidity. By replacing the turbid solution in its absorption cell with distilled water, the transmittancy of the filtered solution may now be measured and calculated to $-\log \mathbf{t}$ to give a measure of color.

Since, in the Balch method, the turbidity value is taken as the difference in $-\log \mathbf{t}$ of a filtered and an unfiltered solution, this value may be similarly obtained with any instrument capable of yielding transmittancy readings at the same wave length. For instruments of the Duboscq type, as previously described (p. 315), where thickness of the absorbing layer is the quantity observed, reliance cannot be placed upon direct matching with a standard, as in filtered solutions, because of the uncertainty of the Lambert law applying to turbid solutions. A procedure may be used with the Duboscq wherein $-\log \mathbf{T}$ for 1-cm thickness of the filtered solution is first found as prescribed, and the latter is then matched against the turbid solution, which is held at fixed thickness. This may perhaps be made more clear by the following example.

The solution (washed raw sugar) was filtered through a loose plug of absorbent cotton and a portion was filtered with asbestos. The absorption of the glass standard, $-\log \mathbf{T}$, at 560 mμ was 0.31069, and the thickness of the filtered solution at match was 1.821 cm. Then $-\log \mathbf{T}$ for $b=1$ cm is $0.31069/1.821=0.17062$. After replacing the filtered solution in one cup with turbid solution, the thickness of the latter in the colorimeter was set at 1 cm, and an intensity match was obtained by adjusting the filtered solution, no standard plate being used. The observed average thickness found was 3.313 cm. Deducting 1 cm, allowance for ordinary absorption in the turbid solution, we have 2.313 cm. Multiplying by $-\log \mathbf{T}$ for $b=1$ cm in the filtered solution, we have $2.313\times0.17062=0.39464$, the value to be called $-\log \mathbf{T}$ for a thickness of 1 cm in the turbid solution. The values for $-\log \mathbf{t}$ are then calculated in the manner prescribed.

2. METHODS EMPLOYING THE ZEISS NEPHELOMETER

(a) DESCRIPTION OF THE APPARATUS

An early design of the Zeiss nephelometer was described by Sauer [2]. The following is a description of a later model, and a diagram of the instrument is shown in figure 81. A more detailed description is to be found in the Zeiss advertising pamphlet [11]:

The apparatus consists of two parts, a Pulfrich photometer in the horizontal position, as shown at the left of the diagram, and a means of producing a Tyndall beam, shown in the circular housing at the right. The cell containing the test liquid is placed in the cylindrical chamber, which contains distilled water. Light from the 8-volt 50-candlepower lamp enters the chamber through a lens as a parallel pencil of square cross section. The light scattered by illuminated particles leaves the chamber through a second lens and enters the left aperture of the photometer in a direction 45° from the direction of incidence. Part of the light from the source is reflected by an inclined glass plate located between the source and the entrance lens, and serves to illuminate an opal or ground-glass diffusing disk which provides a turbidity standard for comparison. Four disks, giving

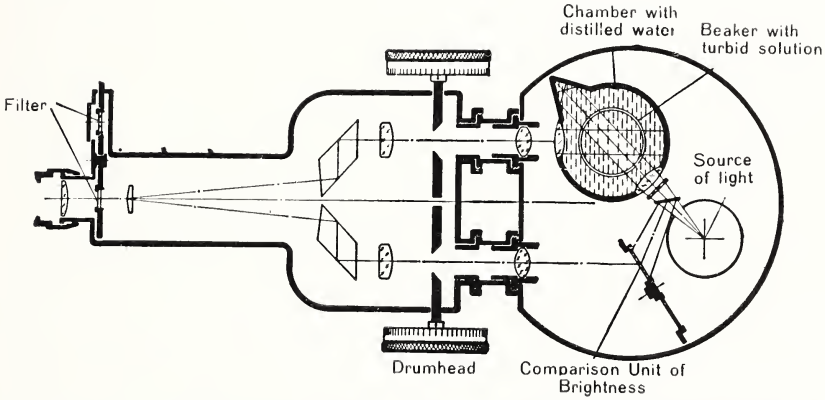

FIGURE 81.—*Zeiss-Pulfrich photometer with arrangements for turbidity measurement.*

different intensities of diffuse light, are mounted in a revolving carrier and are readily interchanged. A translucent glass body with invariable degree of turbidity is provided which may be introduced in the water chamber in place of the sample. This body is calibrated in terms of the incident light and is used for calibrating the instrument and for determining turbidity in absolute terms. In case fluorescing substances are being examined, a red glass is provided to absorb fluorescence-producing radiation from the source. The vessels for containing the test solution consist of a 2.5-mm flat cell of 1-ml capacity and two cylindrical beakers 26 and 36 mm in diameter, respectively, with respective capacity of 10 and 25 ml. Color filters are provided which may be placed in the revolving filter holder of the photometer eyepiece. The green filter is most frequently used because of higher visibility of the transmitted light.

To make an observation, the cell containing the test solution is placed in the water chamber and the corresponding photometer drum set at a reading of 100. One of the standard glass disks is brought into position by rotating the holder; the eyepiece filter is also brought into the field of view. The observer then adjusts the photometer drum corresponding to the position of the turbidity standard (the brightness of the standard should always be greater than that of the sample) until a photometric match is obtained. The

reading of this drum is then in terms of percentage of brightness of the standard. The mean of several readings thus obtained is called the relative turbidity. The calibrated turbid body is now substituted in the water chamber for the sample and in turn matched with the standard disk. The turbidity of the sample in absolute measure follows from the ratio of the two sets of measurements.

Sauer in a second article [3] published a theoretical study of light scattering in which were considered various factors, including the influence of absorption, thickness of layer, direction of observation in relation to direction of illumination, determination of the scattering function from observations, the calibration of turbidity standards, etc.

For the Zeiss-Pulfrich turbidimeter, in which the angle of incidence is 0 and the angle of observation is 45°, Sauer gives for the intensity factor

$$J'=\frac{2}{\sqrt{2}-1}e^{-kd}[1-e^{-kd(\sqrt{2}-1)}],$$

where k is the extinction coefficient (absorbancy) for unit length, d is the thickness of the layer bounded by the parallel surfaces of the plane parallel cell, and e is the base of natural logarithms. Expressed in figures

$$J'=4.83e^{-kd}(1-e^{-kd\ 0.414}).$$

At low concentrations, in turbid media with extinction coefficient up to 0. 01, the effects of multiple scattering are not noticeable. With increasing concentration, multiple scattering or reflection brings about an increasing brightness. Upon reaching a critical concentration the contribution of multiple scattering becomes considerable and finally outweighs the primary scattering by many times. Within the region of concentration wherein multiple scattering causes no noticeable effect, the variation of the observations from the proportionality with kd necessary for calculation may be adjusted by multiplying the observed scattering intensity by the correction factor, $f(k)$. This factor, in the case of observations with the plane parallel cell, may be expressed by the following formula:

$$f(k)=\frac{0.414kd}{e^{-kd}(1-e^{-0.414kd})}.$$

The observations are carried out as already described, the Tyndall beam intensity of the sample being compared with that of the arbitrarily chosen milk-glass plate to obtain the relative turbidity. The calibrated standard with turbidity, t, is substituted for the sample, and its brightness, H, measured against the arbitrary standard. The turbidity, T, or absolute turbidity, is found by the formula

$$T=\frac{\text{relative turbidity}}{H}dt.$$

The factor, d, is equal to the reciprocal relation of the depth of layer in the sample cell to that of the turbid standard. As already explained, t is the absolute turbidity of the glass turbidity standard.

(b) PROCEDURE OF ZERBAN, SATTLER, AND LORGE

Zerban and Sattler [4, 5, 6, 7, 8,] and Zerban, Sattler, and Lorge [9], using the Zeiss-Pulfrich turbidimeter, studied the turbidity of solutions containing coloring matter (caramel) and turbidity (suspended bentonite or Filter-Cel) varied in known proportions. This study was extended to include solutions of raw cane and white refined sugars, one of the objects being to determine both color and turbidity in the turbid solution without filtration.

In preparing the solutions, it is considered imperative that a uniform system be adopted, since a large number of factors can disturb both the color and turbidity values of a given sample. The following procedure is used [4]:

The sugar is weighed in a wide-mouthed Erlenmeyer flask, and enough boiling-hot distilled water is added on the balance to bring the solution slightly above 60 Brix. The flask is placed in a beaker of water at 80° C and the contents is stirred gently. After the sugar is in solution, it is cooled quickly to room temperature and whirled for 15 minutes in a small hand centrifuge at 1,100 rpm to remove coarse material. Finally the density is adjusted to 60 Brix with a refractometer. For dark products the same glass cells are used for measuring both transmittancy and Tyndall-beam intensity, the reference standard for the latter being the turbid glass block, which is calibrated by the manufacturers. After the cells are filled, the optical surfaces are cleaned and polished, and meticulous care is exercised in all manipulations. For nearly colorless solutions the transmittancy must be read in much longer cells, affording thicknesses of 10 to 20 cm. The values of $-\log \mathbf{T}$ may then be reduced to 1 cm or any other desired thickness. Likewise, for low turbidities, the cylindrical cells (26 or 36 mm in diameter) available with the instrument are used.

To find the concentration of turbidity, N, and the concentration of coloring matter, C, from the instrument readings ($-\log \mathbf{T}$ for absorbency, and R for the relative turbidity) two formulas are given [8]:

$$N=\frac{Rf(C)}{a} \tag{90}$$

$$C=(-\log \mathbf{T})-N \tag{91}$$

Combining eq 90 and 91, we have

$$C=(-\log \mathbf{T})-\frac{Rf(C)}{a}, \tag{92}$$

both N and C being expressed as $-\log \mathbf{T}$. $f(C)$ is a correction factor replacing $f(k)$ in the formula of Sauer, $f(C)$ being a function of color alone, whereas $f(k)$ of the Sauer formula is a function of both color and turbidity. The correction factor then becomes

$$f(C)=\frac{\left[(-\log \mathbf{T})-\frac{Rf(C)}{a}\right](\sqrt{2}-1)\times 2.30259}{10^{-\left[(-\log \mathbf{T})-\left(\frac{Rf(C)}{a}\right)\right]}-10^{-\left[(-\log \mathbf{T})-\left(\frac{Rf(C)}{a}\right)\right](\sqrt{2}-1)}}. \tag{93}$$

Although there remains some uncertainty about the true value of constant a, the value found experimentally by the authors ($\log a$ for the green filter=3.77551) is accepted for the present.

To calculate C and N from R and $-\log \mathbf{T}$, eq. 93 is solved for varying values of C, which is the $(-\log \mathbf{T})-Rf(C)/a$ term, and a tabulation of corresponding $f(C)$ values is thus obtained. The substitution of these C and $f(C)$ values at specified increments of R in eq 93 yields a table from which C may be found for any pair of $-\log \mathbf{T}$ and R values. Practically, C is found from curves based on the table, and N is obtained by subtraction from $-\log \mathbf{T}$. A graph covering the entire range of C, $-\log \mathbf{T}$, and R values of raw sugar is shown in figure 82.

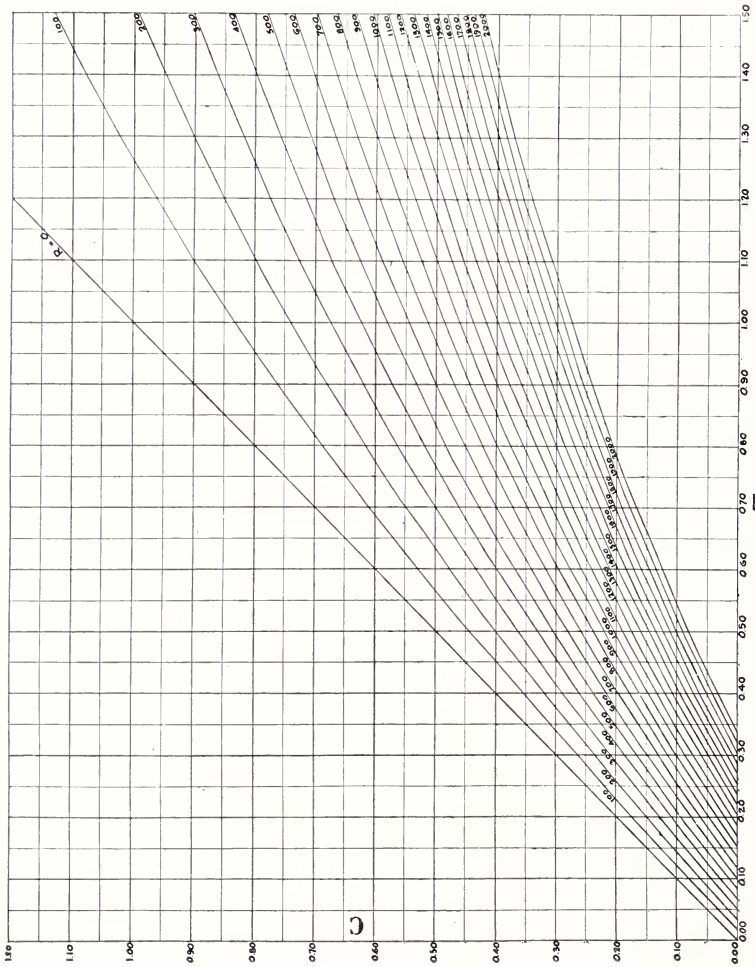

FIGURE 82.—*Zerban and Sattler's curves for finding —log* **T** *and R.*
Full range for white and raw sugars.
—log **T**, absorbancy; C, concentration of coloring matter expressed as —log **T**; R relative turbidity

More exact results may be obtained if interpolation for R is carried out by means of table 41 on the basis of the approximate value of C read from the graph. The use of the table is explained by the following example:

A raw-sugar sample gave $-\log \mathbf{T}=0.57807$, and $R=917.1$ for the green filter. On the graph, C is found to lie between 0.25 and 0.30. The value of $Rf(C)/a$ for 1 R at $C=0.25$ is 0.0003351; hence that for 917.1 R is $0.0003351\times917.1=0.30732$, which, added to 0.25 c, gives

$-\log \mathbf{T}=0.55732$. Similarly the value of $Rf(C)/a$ for 1 R at $C=0.30$, is 0.0003847, and that for $R=917.1$ is 0.35280, which, added to 0.30, gives $-\log \mathbf{T}=0.65280$. The difference, x, between the required value of C and the value 0.25 is found from the equation

$$(x-0.25):(0.30-0.25)=(0.57807-0.55732):(0.65280-0.55732).$$

The result for x is 0.0109, which, added to 0.25, gives a value of 0.2609 for C. N equals $0.57807-0.2609$, or 0.3172.

TABLE 41.—*Zerban and Sattler table for finding C and f(C) from −log* **T** *and R*

C	$f(C)$	$\frac{Rf(C)}{a}$ for $R=1$	C	$f(C)$	$\frac{Rf(C)}{a}$ for $R=1$
0.0000	1.0000	0.0001677	0.1000	1.3200	0.0002213
.0010	1.0027	.0001681	.1500	1.1500	.0002542
.0020	1.0055	.0001686	.2000	1.7406	.0002919
.0030	1.0083	.0001691	.2500	1.9986	.0003351
.0040	1.0110	.0001695	.3000	2.2941	.0003847
.0050	1.0138	.0001700	.3500	2.6331	.0004415
.0060	1.0166	.0001705	.4000	3.0214	.0005066
.0070	1.0194	.0001709	.4500	3.4664	.0005813
.0080	1.0222	.0001714	.5000	3.9757	.0006667
.0090	1.0250	.0001719	.5500	4.5598	.0007646
.0100	1.0278	.0001723	.6000	5.2281	.0008767
.0110	1.0306	.0001728	.6500	5.9937	.0010050
.0120	1.0335	.0001733	.7000	6.8699	.0011520
.0130	1.0363	.0001738	.7500	7.8727	.0013201
.0140	1.0391	.0001742	.8000	9.0199	.0015125
.0150	1.0420	.0001747	.8500	10.3329	.0017327
.0160	1.0448	.0001752	.9000	11.8342	.0019844
.0170	1.0477	.0001757	.9500	13.5520	.0022724
.0180	1.0506	.0001762	1.0000	15.5154	.0026017
.0190	1.0535	.0001767	1.0500	17.7609	.0029782
.0200	1.0564	.0001771	1.1000	20.3270	.0034085
.0220	1.0622	.0001781	1.1500	23.2604	.0039004
.0240	1.0680	.0001791	1.2000	26.6117	.0044623
.0260	1.0739	.0001801	1.2500	30.4415	.0051045
.0280	1.0798	.0001811	1.3000	34.8136	.0058376
.0300	1.0862	.0001821	1.3500	39.8110	.0066756
.0350	1.1023	.0001848	1.4000	45.5150	.0076321
.0400	1.1175	.0001874	1.4500	52.0280	.0087242
.0450	1.1332	.0001900	1.5000	59.4610	.0099706
.0500	1.1488	.0001926	1.5500	67.9469	.0113936
.0550	1,1647	.0001953	1.6000	77.6286	.0130170
.0600	1.1814	.0001981	1.6500	88.6764	.0148696
.0650	1.1978	.0002008	1.7000	101.1057	.0169537
.0700	1.2146	.0002037	1.7500	115.6513	.0193928
.0750	1.2316	.0002065	1.8000	132.0390	.0221408
.0800	1.2491	.0002095	1.8500	150.7322	.0252753
.0850	1.2661	.0002123	1.9000	172.0380	.0288479
.0900	1.2838	.0002153	1.9500	196.3277	.0329209
.0950	1.3017	.0002183	2.0000	224.0030	.0375616

The absolute turbidity can also be calculated by means of table 41 and the Sauer equation

$$S=Af(k)Dt,$$

where S is the absolute turbidity, A is the relative Tyndall beam-intensity as measured with the turbidimeter and equals 0.01 R in the Zerban and Sattler system. D is a factor varying with the thickness of the absorption cell, and t is the absolute turbidity of the standard glass block. By interpolation of column 2 in this table, the $f(C)$ for $C(kd)$ equal to 0.2609 is found to be 2.0630. By substituting this figure in eq 90 along with $A(0.01\ R)=9.171$, $D=6.6395$ (for the

2.455-mm cells used) and $t=0.00282$, the absolute turbidity found is 0.3542.

For products which are low in both color and turbidity the graph shown in figure 83 is used. If the scale is such that C and $-\log \mathbf{T}$ are

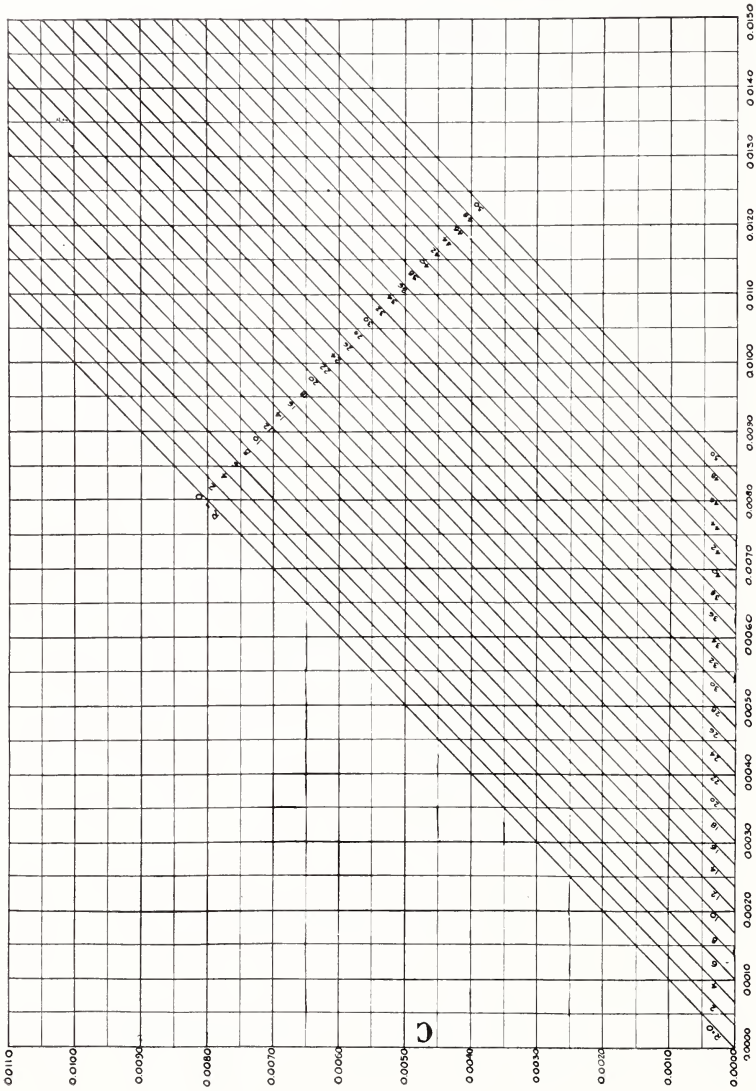

FIGURE 83.—*Enlarged graph of lower portion of figure 82 for products low in both color and turbidity.*

plotted at 50 mm=0.001 unit, it is possible to read C and $-\log \mathbf{T}$ values accurately to the fourth decimal place.

Values of $-\log \mathbf{T}$ and of R, determined at one thickness, may be converted into corresponding values at another thickness, or $-\log \mathbf{T}$ into $-\log \mathbf{t}$. Over a wide range of thickness, the absorbancy is not directly proportional to the depth, b, in the turbid solutions, but is a power function of it, according to the equation

$$-\log \mathbf{T}_1 : -\log \mathbf{T}_2 = (b_1 : b_2)^n.$$

(c) PROCEDURE OF LANDT AND WITTE

Landt and Witte [10], employing a Zeiss-Pulfrich turbidimeter, studied the turbidity in 45-Brix sugar solutions which had been filtered through paper. Only the practical application of their method is given here.

The procedure in making measurements is similar to that of Sauer [3], as described above, in that the turbid solution is first compared in brightness with an arbitrary glass turbidity standard to give the relative turbidity. From this value is deducted the turbidity value of the water surrounding the sample cell, giving a value called the corrected relative turbidity. This value is divided by the brightness of the calibrated turbidity standard, H, of the instrument relative to the turbidity brightness of the arbitrary standard used, thus giving the value A, or $A=$corr. rel. turb./H. The value A is next multiplied by $f(k)$, which, according to Landt and Witte, is found by the Sauer formula, applying only to the plane parallel cells:

$$f(k)=\frac{kd(\sqrt{2}-1)2.303}{10^{-k(d+m+n)}\left[1-10^{-kd(\sqrt{2}-1)}\right]}. \tag{94}$$

Here k is a factor depending upon the extinction coefficient and d is the thickness of layer. For cylindrical beakers, account is taken of the fact that the primary as well as the scattered light suffers a weakening in passage through layers of solution on two sides of the actual Tyndall pencil. These factors are designated, respectively, m and n, and formula 94 becomes for the 26- and 36-mm beakers:

$$f(k)=\frac{kd(\sqrt{2}-1)2.303}{10^{-k(d+m+n)}\left[1-10^{-kd(\sqrt{2}-1)}\right]}. \tag{95}$$

Values of k and f (k), as calculated for various sizes of plane parallel cells are given in table 42, and for the 26-mm and 36-mm beakers, in table 43.

TABLE 42.—*Values of k and f(k) for plane parallel cells of various thicknesses (Landt and Witte)*

Values of k for cell thickness, mm				$f(k)$	Values of k for cell thickness, mm				$f(k)$
1.00	2.50	5.00	10.00		1.00	2.50	5.00	10.00	
0.10	0.04	0.02	0.01	1.030	1.50	0.60	0.30	0.15	1.514
.20	.08	.04	.02	1.061	2.00	.80	.40	.20	1.731
.30	.12	.06	.03	1.087	3.00	1.20	.60	.30	2.335
.40	.16	.08	.04	1.120	4.00	1.60	.80	.40	3.020
.50	.20	.10	.05	1.149	5.00	2.00	1.00	.50	3.970
.60	.24	.12	.06	1.181	6.00	2.40	1.20	.60	5.220
.70	.28	.14	.07	1.216	7.00	2.80	1.40	.70	6.870
.80	.32	.16	.08	1.250	8.00	3.20	1.60	.80	9.020
.90	.36	.18	.09	1.284	9.00	3.60	1.80	.90	11.830
1.00	.40	.20	.10	1.319	10.00	4.00	2.00	1.00	15.190

TABLE 43.—*Values of k and f(k) for cylindrical beakers 26 mm and 36 mm in diameter (Landt and Witte)*

k	$f(k)$ for diameter		k	$f(k)$ for diameter	
	26 mm	36 mm		26 mm	36 mm
0.0004	1.002	1.003	0.0217	1.133	1.172
.0022	1.013	1.016	.0261	1.162	1.210
.0043	1.026	1.033	.0304	1.191	1.250
.0087	1.051	1.066	.0347	1.222	1.290
.0130	1.078	1.100	.0391	1.252	1.332
.0174	1.105	1.136	.0434	1.284	1.375

Next, in order to obtain strict comparison with other plane parallel cells or for calculation to absolute turbidity $Af(k)$ must be multiplied by the factor, D, which is the ratio of the layer thickness of the calibrated standard to the layer thickness of the plane parallel cell. Finally, to reduce the results to terms of absolute turbidity, the whole is multiplied by t, the turbidity of the calibrated standard. The formula is therefore:

$$\text{Absolute turbidity, } T = Af(k)Dt.$$

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XXI. VISCOSITY OF SUGAR SOLUTIONS

1. THEORETICAL

Viscosity is the property of homogeneous fluids that causes them to offer resistance to flow. It is expressed mathematically by the constant of proportionality between shearing stress and rate of shear. It has the dimensional formula $ML^{-1}T^{-1}$, and is generally expressed as η. In the cgs system, the unit of viscosity is the poise. The one-hundredth part of this unit (the centipoise) is frequently used in practice. The viscosity of water at 20° C is often taken as 1.005 centipoises. The ratio of viscosity to density is called the kinematic viscosity, and the cgs unit is called the stoke, poises/(g/cm^3). The reciprocal of viscosity is fluidity. The cgs unit of fluidity is the rhe.

An extensive investigation of the flow in capillary tubes was first undertaken by Poiseuille about 1838. He found that the rate of discharge was directly proportional to the first power of the pressure difference and to the fourth power of the diameter and inversely proportional to the length of the capillary tubes. This relationship, which is known as Poiseuille's law, expressed mathematically, is

$$\frac{V}{t}=\frac{\pi \Delta p R^4}{8\eta L}, \tag{96}$$

where

η=Viscosity, in poises,
V=cm^3 discharge in t (seconds),
Δp=difference in pressure between the two ends of the tube (dynes/cubic centimeter),
L=length of the tube in centimeters,
R=radius of the tube in centimeters.

This formula may be derived, assuming a capillary tube of uniform diameter and sufficiently long that kinetic energy and end effects are negligible. Consider a cylindrical volume element of the fluid of length dL, radius r, and with the difference in pressure dp between the ends. The resultant force tending to push this volume element downstream is $\pi r^2 dp$. This force is resisted by the shearing stresses due to viscosity, assuming the fluid adheres to the walls of the tube. Let S denote the shearing stress at radius r, i. e., the tangential force per unit area exerted upon the cylindrical surface, $2\pi r dL$, by the fluid between it and the wall of the tube. The total shearing force acting upstream is $2\pi r S dL$. Under steady flow conditions (no acceleration), these two forces must be equal, so that

$$2\pi r S dL=\pi r^2 dp. \tag{97}$$

When conditions are uniform throughout the length of the tube,

$$S=\frac{r}{2L}\Delta p. \tag{98}$$

Let v denote the velocity at radius r. The velocity gradient with respect to increasing values of r is $-dv/dr$, where dv is the difference in velocities at the radial distances r and $r+dr$ from the axis of the tube. The definition of viscosity, η, expressed mathematically, is

$$S=-\eta\frac{dv}{dr}. \tag{99}$$

Combining eq 98 and 99 gives

$$dv=\frac{\Delta p}{2L\eta}r dr. \tag{100}$$

The volume of fluid flowing per unit time is $\pi r^2 dv$, and, integrating over the entire tube, using eq 100, gives

$$\frac{V}{t}=\frac{\pi R^4 \Delta p}{8L\eta}, \tag{101}$$

which is the usual form of Poiseuille's law. It also may be written

$$\eta=\frac{\pi R^4 t \Delta p}{8LV}=Ct\Delta p, \tag{102}$$

where $C=\pi R^4/8LV$ is a constant for a given capillary viscometer. Where the liquid of density, ρ, flows by gravity with an effective

hydrostatic head, h, so that $\Delta p = \rho h g$, eq 102 gives for the ratio of viscosities of two liquids

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 h_1 t_1}{\rho_2 h_2 t_2}. \tag{103}$$

Equations 102 and 103 have been accurately verified experimentally for long capillaries with small rates of flow. The results of measurements over a convenient range of rates of flow with many types of capillary viscometers have been found [1,2, 3] to be represented, within experimental errors, by the relation

$$\eta = At\Delta p - \frac{B\rho}{t}, \tag{104}$$

where A and B are instrumental constants for a particular viscometer and direction of flow. The constant B has been found to be approximately equal to $V/8\pi L$ (using cgs units in eq 104), but it should be determined by experiment.

2. CAPILLARY-TUBE VISCOMETERS

(a) OSTWALD VISCOMETER

The Ostwald viscometer (fig. 84–I) is one of the earliest forms. It consists of a glass U-shaped tube, one limb of which contains a smaller bulb discharging into a capillary tube, while the other contains a tube of larger diameter with a larger bulb near the bottom. There are no standard dimensions for this instrument, and since the hydrostatic head causing flow cannot be varied, any considerable change in viscosities must usually be covered by the use of a series of instruments with capillaries of different sizes. With the usual type of Ostwald viscometer, a certain volume of liquid is introduced into the wider limb, frequently by means of a pipette, and drawn up through the capillary to a mark above the smaller bulb. In making a measurement with all Ostwald instruments, the liquid is forced through the capillary tube to a mark above the upper bulb, and the time required for the meniscus to fall by gravity from the upper mark, C, to another mark, D, below the bulb, is measured.

(b) BINGHAM VISCOMETER

The Bingham viscometer (fig. 84–II) is a refinement of the Ostwald capillary tube type. An advantage is the small sample required, 4 ml being a common capacity of the bulb, C, which is emptied or filled during a measured time interval. There are no standard dimensions, the range of viscosities to be measured determining the size of capillary chosen. Any one instrument can be used to measure a wide range of viscosities, since various pressures may be used. The average hydrostatic head may be made negligible, the liquid being forced through the capillary by air pressure, which is kept as constant as possible during a measurement. A trap makes it possible to take readings at increasing temperatures without refilling. The working volume of liquid is from A to H or from E to M. Drainage errors may be avoided by forcing the liquid through the capillary into a dry bulb, in which case the time required for the meniscus to pass from D to B is measured.

(c) UBBELHODE VISCOMETER

The Ubbelhode viscometer (fig. 84–III) is a "suspended level" instrument [5]. It consists essentially of three glass bulbs connected by suitable tubes, one of which is a capillary. The pipette, A–D, provided with graduations at M_1 and M_2, connects through the capillary, 4, with the 12-mm bulb, C. The bulb, C, is connected with bulb, B, and to the atmosphere through tube 3. Bulbs A and B are connected to the atmosphere through tube 2 and the larger filling tube, 1, respectively.

In operation, bulb B is filled with the liquid in question through tube 1 until the meniscus lies between the marks X and Y. Tube 3

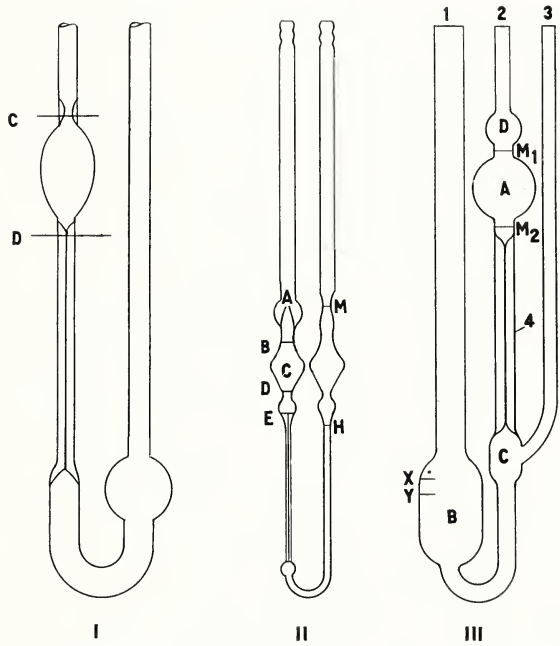

FIGURE 84.—*Viscometers.*

I, Ostwald; II, Bingham; III, Ubbelhode.

is closed at the top, and suction is applied to tube 2 until the liquid is drawn above the mark M_1. Tubes 2 and 3 are now opened to the atmosphere, thereby dividing the liquid in C into two parts and producing the "suspended level" at the lower end of capillary 4. Simultaneously with the formation of the suspended level, the liquid begins to flow in a thin layer on the vertical walls of C into B. The observer determines the interval of time required for the meniscus to drop from M_1 to M_2.

3. SHORT-TUBE VISCOMETERS

There are a number of short-tube efflux viscometers, such as the Saybolt (United States), Redwood (Great Britain), and Engler (Germany), sufficiently alike to be considered as a group. These

instruments have been widely used in the petroleum industry. The dimensions of each instrument and the methods of operation have been standardized in different countries. They are sturdy, since they are constructed almost entirely of metal, and are easily manipulated. The instruments are portable and require no elaborate installation other than provision for heating the bath. The operation of each instrument is essentially the same. The liquid to be examined is poured into an open cup or tube, in the base of which is a short capillary provided with a simple form of valve. The level of the liquid in the cup is adjusted to a definite height, the valve is opened, and an observation is made of the time required for a definite volume to be discharged through the air into a measuring vessel placed below the capillary.

4. FALLING-BALL VISCOMETERS

Viscosity may also be measured by determining the velocity with which a sphere of known radius falls in a viscous medium. The relation between the viscosity; density of the liquid, ρ; density of the sphere, ρ_b; velocity of the sphere, V; and radius of the sphere, R, according to Stokes' Law, is

$$\eta=\frac{2(\rho_b-\rho)gR^2}{9V}. \tag{105}$$

In this equation the velocity of the sphere is assumed to be constant, and no consideration is given to effects of the walls and ends of the vessel. Experimental evidence [3] indicates that corrections for such effects are practically independent of the viscosity, so that for a given tube and sphere which falls the same distance in times t_1 and t_2 in two different liquids, 1 and 2, the ratio of the viscosity is given by

$$\frac{\eta_1}{\eta_2}=\frac{(\rho_b-\rho_1)}{(\rho_b-\rho_2)}\frac{t_1}{t_2}. \tag{106}$$

(a) HOEPPLER VISCOMETER

The Hoeppler viscometer is a modification of the falling-ball type. It consists of a glass tube of uniform internal diameter mounted at a 10° angle from the vertical, through which a ball is allowed to roll. Balls of different sizes are available, so that this instrument is applicable to a large range of viscosities (0.6 to 75,000 centipoises). Measurements of the time required for a ball to pass between the two marks on the glass tube when it is filled with different liquids permit an evaluation of viscosity by means of eq 106.

5. ROTATIONAL VISCOMETERS

The resistance which a liquid offers to a rotating body may also be used to measure the viscosity of that liquid. The MacMichael and Stormer viscometers, which have been used largely with liquids having viscosities greater than about 1 poise, belong to this type of instrument.

(a) MacMICHAEL VISCOMETER

The MacMichael viscometer [6] consists essentially of a motor-driven cup in which the bob of a torsional pendulum is suspended. When the cup is rotated at a constant speed the pendulum is deflected

until the viscous drag of the liquid is balanced by the resistance of the suspended wire to twisting. When the pendulum has come to rest a reading may be made. Each instrument is supplied with a number of wires of different sizes, so that a wide range of viscosities may be determined with this instrument. The pendulum is provided with a graduated disk divided into 300 equal parts called MacMichael degrees. Viscosity in poises may be calculated by the following formula:

$$\eta = K\frac{M^\circ}{HN}. \tag{107}$$

where K=instrument constant,
M°=deflection in MacMichael degrees,
H=depth of submergence of the pendulum bob in centimeters,
N=number of revolutions per minute of the cup.

(b) STORMER VISCOMETER

The Stormer viscometer consists of a central rotor and a stationary concentric cylinder containing the liquid whose viscosity may be determined, after suitable calibration of the instrument, from measurements of the time required for completing a definite number of revolutions of the rotor immersed in the sample and driven by a definite weight.

6. CALIBRATION OF VISCOMETERS

Most of the viscometers used in routine determinations of viscosity require careful calibration in order to obtain accurate values for viscosity in absolute units. Such calibrations involve essentially the determination of certain instrumental constants which appear in the particular form of equation found to be applicable to a given type of instrument. With capillary tube instruments, in which the average pressure difference depends upon the average hydrostatic head, h, and $\Delta p = \rho h g$ in eq 102, the viscosity, in absolute units, may be calculated from

$$\eta = A\rho t - \frac{B\rho}{t}, \tag{108}$$

where ρ is the density of the liquid in grams per cubic centimeter, t is the time in seconds for a definite volume of flow, and A and B are instrumental constants for a certain temperature and procedure. Similarly, with falling-ball or rolling-ball instruments, the following form of equation may be used:

$$\eta = C(1-\rho/\rho_b)t, \tag{109}$$

where ρ and ρ_b are the densities in grams per cubic centimeter of the liquid and ball, respectively; t, in seconds, is the time of fall of a certain ball between definite marks on a given fall-tube; and C is an instrumental constant applicable to that ball and tube for a certain temperature and procedure. This equation permits the calculation of viscosity in absolute units.

The above equations and analogous relations for other types of viscometers are known to apply only to conditions called streamline or viscous flow and are not applicable when the flow becomes turbu-

lent. It is advisable, therefore, not to use a rate of flow in any viscosity determination which exceeds the maximum employed in the calibration of the instrument. Positive assurance of the applicability of such equations with evaluated constants can be obtained from calibrations covering the entire range of viscosities to be determined. Some instruments require occasional recalibration to eliminate errors caused by corrosion and other effects.

While the instrumental constants depend very largely on the dimensions of the instrument, they may also depend to some extent on the procedure and the physical properties of the liquids employed. The constant A in eq 108, for example, may be somewhat different for two liquids of widely different surface tension or viscosity, since the actual working pressures or the volumes of flow between two works may be different in the two instances. In measurements much above or below room temperatures with some instruments, alterations in procedure and differences in the heat capacity and thermal conductivity of different liquids may alter the effective value of the instrumental constants in addition to the effect of temperature on the dimensions of the instrument.

Instrumental constants may be determined from measurements with one or more liquids of accurately known viscosity and density. Errors in subsequent viscosity determinations may be practically eliminated by employing for calibration purposes liquids with physical properties not very different from the liquids to be investigated. It is for this reason that the data on pure sucrose solutions are especially useful in calibrating viscometers employed in the sugar industry. Distilled water is very frequently used, but its viscosity is so low as to be outside the practical range of some viscometers. In any case, it is always desirable that calibrations with water be supplemented by calibrations with more viscous liquids. A convenient method of determining A and B in eq 108 is to plot $\eta/\rho t$ against $1/t^2$ for several calibrations. The value for A is obtained from the intercept at $1/t^2=0$, and B is obtained from the slope of the best straight line representing the measurements.

One factor limiting the accuracy of calibrations is the measurement of time. Other factors, when using sucrose solutions, are the purity of the sucrose and the concentration of the solution. Many laboratories have water and sucrose of high purity available and are equipped with balances which permit the preparation of solutions whose concentration in a given vessel can be accurately measured to better than 0.01 percent by weight in vacuo. Such solutions may contain a small amount of solid particles resembling dust or lint. It is better to make several calibrations, discarding results obviously affected by such particles, than to resort to filtration, which may change the initial concentration by an unknown amount. Precautions should be taken to ensure that the initially measured concentration remains unchanged. If the solution is not used during the day of preparation, the vessel and contents should be reweighed and a correction applied to the initial concentration, if necessary. Before transfer to the viscometer, the solution should be stirred by shaking gently and mixed with any condensate on the upper walls of the vessel. Special care should be taken to avoid evaporation or condensation of water during transfer and subsequent calibration measurements.

Another important factor is the control and measurement of temperature. It may be noted that data on pure sucrose solutions contained in table 130, p. 671, and recommended for use in calibrations are limited to the temperature range 15° to 25° C because of the difficulty of avoiding condensation or evaporation outside this range of temperature. The data in table 130, together with the accepted value for water at 20° C, permit calibrations over the range 1 to 4,000 centipoises, which should be consistent to the order of 0.1 percent or comparable to the accuracy attainable in the major factors, namely timing, temperature, and concentration.

7. VISCOSITY OF VARIOUS SUGAR SOLUTIONS

(a) SUCROSE

Measurements of the viscosity of aqueous solutions of pure sucrose have been reported by many experimenters. In 1917 Bingham and Jackson [7] published measurements over the range 0° to 100°C on solutions containing 20, 40, and 60 percent of sucrose, and reviewed the results of several earlier observers. Landt [8] reviewed most of the data published up to 1936 and compared his measurements with the data of various authors on solutions containing 60 to 84 percent of sucrose. These two articles supply a fairly complete bibliography on the subject and indicate differences of several percent in general between the results reported by different experimenters.

This lack of agreement, together with indirect evidence that some of the interpolated values given by Bingham and Jackson were in error by several percent, led to a further investigation at this Bureau.[19] Viscosity measurements were made over the range 0° to 35° C on solutions containing 30, 40, 50, 60, 65, 70, and 75 percent by weight in vacuum. These solutions were initially prepared with a precision of better than 0.001 percent in the concentration, using sucrose of very high purity. Changes in the initial concentration during the filling of the viscometers were minimized by special precautions described in the previous section on the calibration of viscometers. Three instruments similar to the one described by Bingham and Jackson [7] were employed with capillaries of different diameters. The instrument with the smallest capillary was calibrated with water at 20° C, assuming the value 1.0050 centipoises. The calibrations of the other instruments were carried out with several liquids of higher viscosity in a step by step process. Drainage errors were eliminated by always flowing the liquids into a dry bulb. A separate sample was used for each viscosity determination. At least two measurements, usually agreeing to 0.1 percent or better, were made at each temperature, which was adjusted to the desired integral temperature (indicated by a platinum resistance thermometer) and usually maintained constant to less than 0.01° C.

The unpublished results described above have been used as the major basis for tables 130, 131, 132, and 133, pp. 671-75. Above 35° C, the tabulated data are based largely on the results of Bingham and Jackson [7], Landt [8], and Bennett and Nees [9]. Recalculation of Landt's data, using slightly higher values for the constants for his falling-ball viscometers, evaluated from data on 60-percent sucrose

[19] The results of this investigation will be published separately in the Bureau's Journal of Research.

at 20° and 30° C, leads to very satisfactory agreement between these three groups of observers.

Jones and Stauffer [10] made some very precise viscosity measurements on aqueous solutions at 25° C and obtained 5.8168 for 40-percent sucrose and 1.9106 for 20-percent sucrose relative to water at 25° C, which give for the ratio $\eta_{40}/\eta_{20}=3.0445$. The values given in the tables at 25° C yield for this ratio $\eta_{40}/\eta_{20}=5.199/1.706=3.0475$, the two ratios agreeing to 0.1 percent.

Mühlendahl [11], in a paper on sucrose solutions as calibration liquids for viscometers, reported values for the viscosity of 60- to 66-percent sucrose solutions, which are 10 to 20 percent lower than the values in table 130, p. 671. His data are also reported in Landolt-Börnstein [14]. Mühlendahl calibrated his Ostwald-type viscometer with water over the range 14°to 30° C, assumed Poiseuille's law, and represented the assumed single instrumental constant as a function of temperature, which was used erroneously in the calculations of the viscosity of sucrose solutions from the observed time of flow. Recalculation of his data, using the method of calibration outlined in the previous section to obtain two instrumental constants, indicates that his observations are consistent with the data in table 130 to the order of 1 percent.

A critical examination of the data reported by various authors indicates that most of the measurements on sucrose solutions are consistent with the data in tables 130, 132, and 133, within reasonable uncertainties in the calibrations and in the measurements of time, temperature, and concentration. It seems probable that the greatest uncertainty in many instances was the concentration of the solution at the time of the viscosity measurement.

(b) MISCELLANEOUS

International Critical Tables [15] gives a compilation of data of various investigators on the viscosity of aqueous solutions containing less than 50 percent by weight of pure sugars, including dextrose, levulose, galactose, lactose, maltose, raffinose, and several mixtures of sucrose and dextrose and also of sucrose and levulose. For a given total concentration of sugar at a given temperature, the viscosities of all of these solutions are of the same order of magnitude as pure sucrose solutions.

Orth [12] reported measurements from 20° to 90° C on impure beet sugar solutions containing 60 to 80 percent of total solids which ranged from 65 to 100% sucrose. He found that the nonsucrose present in such solutions was equivalent, on the average, to about 0.97 of the same weight of sucrose and that the viscosities of solutions of equal total dry substance were approximately equal at the same temperature.

Bennett and Nees [9] reported the same approximate relationship for various beet-sugar sirups. They found that the viscosity of steffanized and nonsteffanized sirups with equal total dry substance decreased approximately linearly with increased nonsucrose content. On the other hand, the viscosity of high raffinose sirups of equal dry substance was found to increase with the nonsucrose content.

Spengler and Landt [13] determined the influence of 14 different inorganic salts on the viscosity of a saturated sucrose solution at 20° C. On the addition of 2 to 10 percent by weight, nine of the salts increased the viscosity, while the other five salts decreased the viscosity.

Viscosity is an important factor in processes of diffusion and crystallization and in practical problems involving the flow of fluids. In the design of pipe lines for handling sirups and molasses only an approximate value of the viscosity is required. The data in tables 132 and 133, p. 673-74, may be useful in such cases if the total dry substance is known.

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XXII. SOLUBILITY OF THE COMMON SUGARS

1. SOLUBILITY OF SUCROSE IN WATER

The solubility of sucrose in pure water has been measured by a number of investigators. Their results are not in entirely satisfactory agreement. Sucrose in the final stages of solution or deposition from supersaturated solution attains equilibrium very slowly, and it is difficult to arrive at the same result from both directions, which must be considered the criterion of accuracy. Many of the calculations of supersaturation coefficients of industrial sirups are based on the solubility of pure sucrose as determined by Herzfeld [1], whose data are given in table 134. The solubility as determined by other workers is given in table 135.

On the basis of Herzfeld's table of solubility of sucrose, Kukharenko [2] has calculated the supersaturation and crystallization velocity shown in table 136. p. 677. The table also includes data on concentration, oversaturation, and hypothetical yield.

2. SOLUBILITY OF DEXTROSE IN WATER [3]

An aqueous solution of dextrose in contact with an excess of α-dextrose crystals reaches equilibrium slowly, whether the latter is approached from undersaturation or supersaturation. This is due not only to the fact that, in common with many other substances, equilibrium between crystals and solution is attained slowly, but also to the fact that final equilibrium cannot be attained until mutarotation of α- to β-dextrose is complete. The final saturated solution is thus an equilibrium between dextrose crystals and dissolved α-dextrose which is in equilibrium with β-dextrose. The rates of mutarotation of dextrose are given on page 763.

Dextrose occurs in two crystalline forms, the monohydrate and the anhydrous. The monohydrate is the stable phase between the cryo-

hydric point −5.3° and 50° C. Above 50° C the anhydrous form becomes stable and remains so until, in the vicinity of 100° C, the β-dextrose becomes stable. The anhydrous form can exist at temperatures considerably below 50° C if the crystals are uncontaminated by the hydrate. Indeed, it is possible to obtain the crystalline anhydrous form by cooling the massecuite to below 30° C.

The solubility data are given in table 137, p. 679, and plotted in figure 85. Curve II shows the approximate instantaneous solubilities

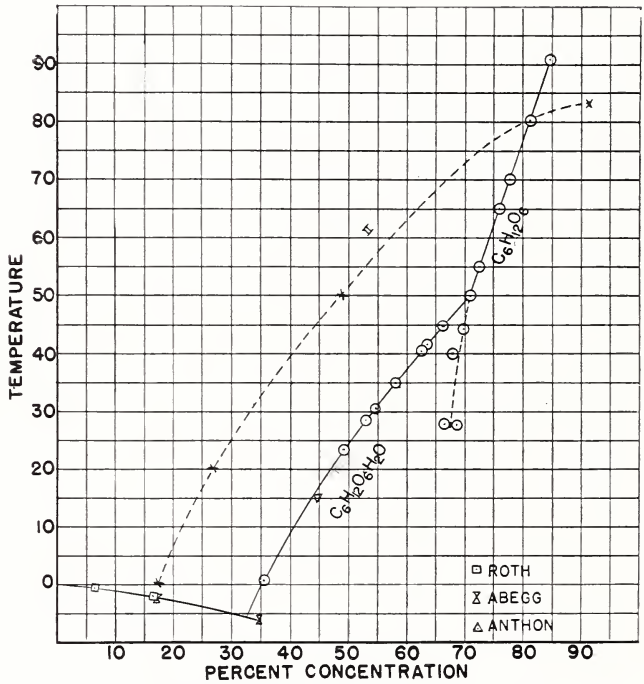

FIGURE 85.—*The system dextrose and water.*

The solid curves show the final equilibria with respect to the solid phases, ice, dextrose hydrate, and anhydrous dextrose. The dotted curve shows the instantaneous solubility before mutarotation. All data are expressed in terms of anhydrous dextrose.

of α-dextrose hydrate, in which the solid phase is in momentary equilibrium with α-dextrose in solution before mutarotation to β-dextrose has begun. This curve passes through the melting temperature of the hydrate, at which temperature the solution has the same composition as the crystals.

3. SOLUBILITY OF LEVULOSE IN WATER

The solubility of levulose was determined at three temperatures by Jackson, Silsbee, and Proffitt [4] as an adjunct to experiments on the crystallization of the sugar from aqueous solution. If a parabolic form of the solubility curve is assumed, the solubility at temperatures intermediate between the determined points can be computed by the formula

$$C=0.150103t^2-0.814t+331.023,$$

in which C equals the weight of levulose in 100 g of water and t is the centigrade temperature. Such calculated points must be considered as approximations. The solubilities are given in table 138.

In order to encourage and facilitate studies on the crystallization of levulose, an extended table of concentration and supersaturation (table 139, p. 682) has been computed. These data are admittedly based on insufficient experimental work and must be considered purely tentative.

4. SOLUBILITY OF LACTOSE IN WATER

Lactose occurs in alpha and beta forms, the alpha form crystallizing with 1 molecule of water, and the beta in the anhydrous state. The transition temperature between the two forms is 92° to 93° C; below this temperature the alpha hydrate separates from a supersaturated solution, whereas the anhydrous beta form crystallizes at temperatures above.

Table 140, p. 690, published by Gillis [5], contains the experimental results of Hudson [6], Saillard [7], and Gillis [8]. The first two authors approached the saturation point from both supersaturated and undersaturated solutions. Hudson determined the amount of lactose present by evaporating the solution and drying the crystalline residue at 130° C. to constant weight. Saillard employed polariscopic and copper-reduction methods of analysis, which he standardized by drying the lactose on sand at 105° to 106° C. Gillis approached the saturation point by increasing the temperature of a solution in the presence of a solid phase until the disappearance of all crystals.

Hockett and Hudson [9] have found that when the alpha lactose hydrate is shaken for 10 minutes at room temperature with 10 times its weight of methyl alcohol containing from 2 to 5 percent of anhydrous hydrogen chloride, a crystalline phase separates. This is a molecular compound having the composition 5 α-lactose–3 β-lactose.

5. SOLUBILITY OF SUGARS IN SUGAR MIXTURES

(a) THREE-COMPONENT SYSTEMS

The system: dextrose, levulose, and water.—When a sugar is dissolved in an aqueous solution of another sugar, its solubility in the water of such a solution is in general diminished as a result of the salting-out effect of the second sugar. Thus Jackson and Silsbee [10], in a study of the solubility of dextrose in levulose solutions, found that while 100 parts of pure water dissolved 120.5 parts of dextrose (anhydrous) at 30° C, 100 parts of water containing 106.2 parts of levulose dissolved but 114.8 parts of dextrose. Compared with other systems described below, this is but a slight diminution of solubility. The solid phase in these equilibria is crystalline dextrose containing 1 molecule of water of crystallization.

Systematic data obtained by Jackson and Silsbee are given in table 142, p. 691, and plotted in figure 86. In this figure the point E represents the solubility of pure dextrose in water at 30° C, that is, 54.64 percent, the solid phase being α-dextrose hydrate. Curve EG shows the solubility of dextrose in the presence of increasing concentrations of levulose, while the straight line, EI, represents constant relations between dextrose and water. The departure of solubility curve EG from EI is seen to be slight.

The line KL bisects the diagram, and is therefore the locus of all solutions in which the ratio of dextrose to levulose is unity. In other words, it is the locus of all invert-sugar solutions. At the intersection F of the line KL with the dextrose solubility curve EG we have the point which represents the composition of a solution which is saturated with dextrose and which contains 34.85 percent of dextrose and 34.85 percent of levulose. In other words, this point represents the "solu-

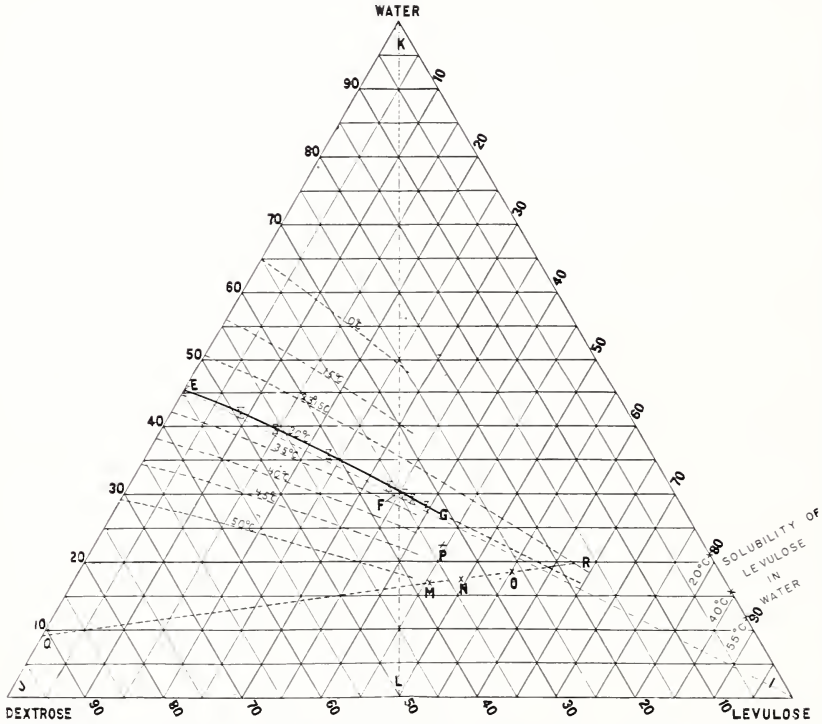

FIGURE 86.—*The system dextrose, levulose, and water.*

EG is the saturation curve of dextrose in the presence of levulose determined experimentally. The dotted curves extending from the *KJ* coordinate are similar curves computed. The line *KL* is the locus of all invert sugar solutions. The intersections of the dextrose saturation curves with *KL* represent the compositions of invert sugar solutions saturated at the respective temperatures with dextrose. *M*, alfalfa honey; *N*, sage honey; *O*, tupelo honey; *P*, Cuban honey. *X*'s on the water-levulose line show the solubilities of levulose at 20°, 40°, and 55° C, respectively.

bility" of invert sugar, if "solubility" is understood to have the significance that a solution containing 69.7 percent of invert sugar is saturated at 30° C with respect to dextrose.

Since the salting-out effect of levulose is small, it is possible to compute without serious error the solubility of invert sugar at other temperatures by assuming a similar departure of the solubility curve from the straight line joining the point I with the solubility of dextrose in water at the respective temperatures. These computed solubilities are given in table 141, p. 691, and plotted as dotted lines in figure 86.

The data presented here represent the system after attainment of equilibrium. Equilibrium is approached very slowly even in the presence of abundant quantities of the solid phase. If the solid phase is not present, the solutions may remain supersaturated for long

periods. Honey is essentially a mixture of dextrose and levulose, with the latter usually in excess. Jackson and Silsbee [10] have calculated from the analyses of Browne [11] and Bryan [12] that all the honeys for which analyses were available were supersaturated with respect to dextrose. In those calculations, the small content of nonsugars was disregarded and the small quantity of sucrose was added arithmetically to the levulose, since the effects of these two sugars on the solubility of dextrose were approximately the same. Proceeding in this manner, they found that 92 American honeys analyzed by Browne had an average supersaturation coefficient of 2.42 at 23° C

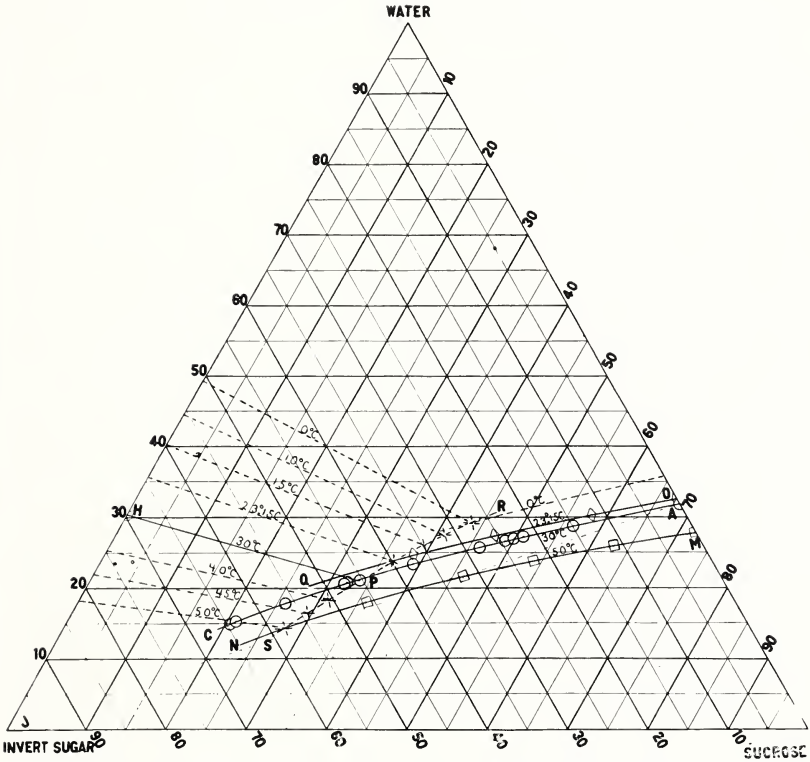

FIGURE 87.—*The system sucrose, invert sugar, and water.*

MN, *AC*, and *OQ* are saturation curves of sucrose in the presence of invert sugar. *HP* is the composition of invert sugar saturated with dextrose in the presence of sucrose. *P* is the composition of a mixture of sucrose and invert sugar saturated with sucrose and dextrose at 30° C. *RS* represents the variation of *P* with temperature. Solid lines are experimental; dotted lines are computed.

with respect to dextrose and a ratio of levulose to dextrose of 1.19. The 72 imported honeys analyzed by Bryan had an average supersaturation of 1.90 and a ratio of 1.20. The points M, N, O, and P in figure 86 represent the composition of certain characteristic honeys. Points M, N, and O, by coincidence, lie on the line QR, Q being the composition of crystalline dextrose hydrate. If in any of these honeys dextrose starts to crystallize, say, for example, at 23.15° C, the solution becomes more and more impoverished with respect to this constituent, and its composition moves to the right on the line QR until it becomes

just saturated at R with respect to dextrose. For honey M, the relative quantities of the resulting phases are proportional to the lengths of the segments JM (solution) and MR (crystals). All honeys are probably supersaturated with dextrose, and the fact that they can be kept in fluid form for considerable periods of time is due to the sluggishness with which the sugars crystallize.

(b) SOLUBILITY OF SUCROSE IN INVERT-SUGAR SOLUTION

Van der Linden [13] first showed that the solubility of sucrose in the water of an invert-sugar solution was less than in pure water.

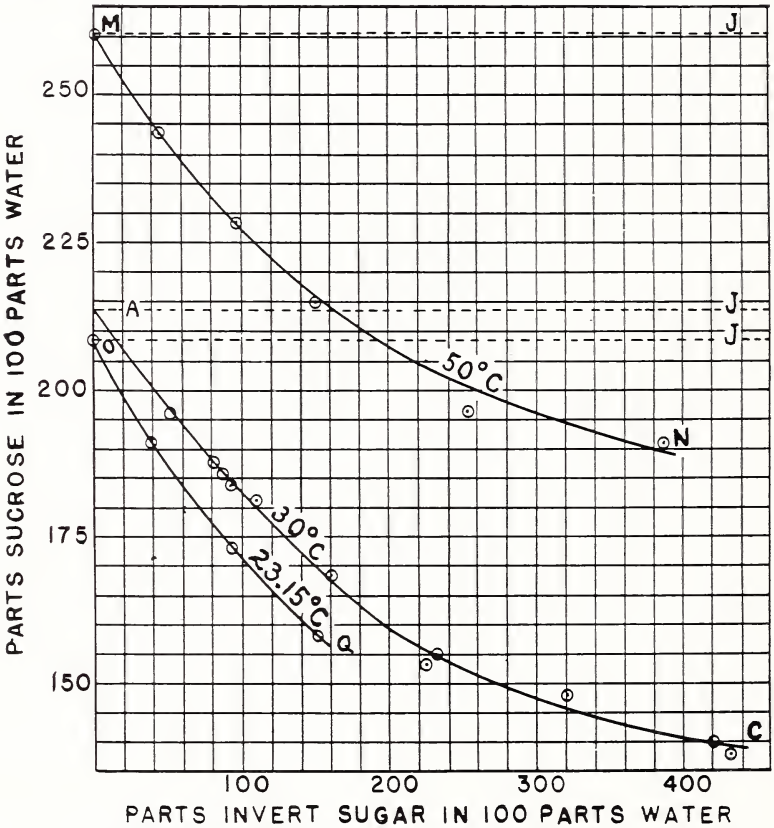

FIGURE 88.—*The system sucrose, invert sugar, and water.*

The solubilities of sucrose at 23.15°, 30.0°, and 50.0° C in the presence of varying amounts of invert sugar. The solubilities are calculated to a constant water content. The lines *AJ*, *MJ*, and *OJ* are the loci of all solutions having a constant ratio of sucrose to water.

Jackson and Silsbee [10] measured these solubilities with precision at 23.15°, 30.0°, and 50.0° C. Their measurements are shown in table 143, p. 692, and plotted in curves OI, AC, and MN in figures 87 and 88. The salting-out effect is shown best in figure 88 in which, if no such effect occurred, the solubilities calculated to 100 parts of water would have followed the horizontal dotted lines.

As the concentration of invert sugar is increased, the saturation point of dextrose is ultimately reached, and at complete equilibrium

dextrose would crystallize from this system upon further increase of concentration of invert sugar. At this point the solution is saturated with both sucrose and the dextrose constituent of the invert sugar and is thus the concentration of maximum solubility which a mixture of sucrose and invert sugar can have. At 30° C this is plotted as point P in figure 87. The sirup of maximum solubility contains 33.57 percent of sucrose and 45.44 percent of invert sugar.

As shown in table 141, p. 691, the solubility of invert sugar varies considerably with temperature, and therefore the composition of the sirup of maximum solubility varies with temperature. This change in composition can be computed with fair approximation, and is plotted on the curve RS in figure 87, and is also given numerically in table 144, p. 692.

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XXIII. BOILING POINTS OF SUCROSE SOLUTIONS

1. GENERAL

When, for the purpose of controlling boiling operations, the concentration of a solute in a boiling liquid is to be determined, it is more conveniently found from the relationship existing between the boiling-point elevation and concentration of dissolved substances than by direct determination. Heretofore, Claassen's [1] boiling-point elevation table for aqueous solutions of sucrose has been used in this manner throughout the sugar industry and in laboratories. His table has been subjected to some criticism [*2*], however, owing to the fact that his values, determined at a pressure of 760 mm Hg, do not take into account the effect of variations in pressure on the boiling-point elevation. As a result of this criticism, and at Claassen's own suggestion, Spengler, St. Böttger, and Werner [3] determined the boiling-point elevation of pure and impure sugar solutions at various concentrations under numerous conditions of pressure. From these observations they plotted curves and from the curves selected values of boiling-point elevations corresponding to even values of Brix for each pressure and purity condition, from which they erected a table covering pressures ranging from ¼ to 2 standard atmospheres and concentrations ranging from 15 to 90 percent of solids.

It was thought that for the purpose of constructing table 145, p. 694, it would be well to correlate Spengler's observed data by means of empirical equations rather than to use the graphic method.

By means of such equations, it is not only easy to calculate a table which is interpolated readily but also to obtain other special values not given in the table. Furthermore, values from the equation may be compared with observed data.

It is interesting to note that in most cases values calculated from these equations agree with Spengler's observed data better than they do with his graphic data; therefore, the use of such equations throughout the range of observed concentrations is justified. These equations are as follows:

100 purity

$$\log_{10} \Delta t = 2.6157 \times 10^{-6} X^3 - 4.0185 \times 10^{-4} X^2 + 4.2567 \times 10^{-2} X - 1.1979,$$

90 purity

$$\log_{10} \Delta t = 3.1013 \times 10^{-6} X^3 - 5.1209 \times 10^{-4} X^2 + 4.9574 \times 10^{-2} X - 1.2622,$$

80 purity

$$\log_{10} \Delta t = 2.9431 \times 10^{-6} X^3 - 4.8211 \times 10^{-4} X^2 + 4.7512 \times 10^{-2} X - 1.1533,$$

70 purity

$$\log_{10} \Delta t = 3.3138 \times 10^{-6} X^3 - 5.5257 \times 10^{-4} X^2 + 5.1177 \times 10^{-2} X - 1.1305,$$

where Δt is the boiling-point elevation of the solution above that of pure water at a pressure of 1 standard atmosphere, and X is the concentration in percentage of solids.

Knowing the boiling-point elevation at 1 atmosphere (Δt_{160}), the boiling-point elevation at another pressure (Δt_p) may be calculated by means of the following equation:

$$\Delta t_p = \Delta t_{760} \left(\frac{T_p}{T_{760}} \right)^2 \frac{L_{760}}{L_p}. \tag{110}$$

This is the same as eq. 127, the derivation of which is given on the following pages.

2. DEFINITION OF BOILING POINT

The boiling point of a liquid may be defined as the temperature at which its vapor pressure is equal to the pressure of the surrounding atmosphere [4]. If the liquid is considered as a solution of two substances, A the solvent and B the solute, then the total vapor pressure is equal to the sum of the partial vapor pressures resulting from A and B. If, however, the solute B is as nearly nonvolatile as sugar, the total vapor pressure is that arising from the solvent only and depends on the number of solvent molecules present in the vapor phase per unit volume.

3. RELATIONSHIP BETWEEN VAPOR PRESSURE AND CONCENTRATION OF SOLUTE IN A LIQUID

According to the law of Raoult, a definite relationship exists between the number of molecules present in the vapor phase and the number of the same molecular species present in the liquid phase. The vapor pressure of a liquid, p, is proportional to x_0, the mole fraction of the liquid which exists in the form of the same molecular species as the vapor, or

$$p = kx_0. \tag{111}$$

If we consider the pure solvent by itself, in which case the same molecular species exists in both the liquid and vapor phases, then the mole fraction, x_0, becomes unity, and we have the proportionality factor, k, equal to the vapor pressure, p_0, or

$$k=p_0, \tag{112}$$

and from eq 109

$$p=p_0x_0. \tag{113}$$

Substracting both sides of eq 113 from p_0, we have

$$p_0-p=p_0-p_0x_0. \tag{114}$$

Dividing eq 114 by p_0, there results

$$\frac{p_0-p}{p_0}=1-x_0. \tag{115}$$

However, by definition, x_0 is the mole fraction of solvent present in the liquid, or

$$1-x_0=1-\frac{N_0}{N_0+N}=\frac{N}{N_0+N}, \tag{116}$$

which, substituted in eq 115, gives

$$p_0-p=p_0\frac{N}{N_0+N}=p_0x, \tag{117}$$

in which x is the mole fraction of solute present in the solution, N refers to the number of moles of solute present which have the molecular weight of the solute, and N_0 is the number of moles of solvent present which have the molecular weight of the solvent in the vapor state.

4. RELATIONSHIP BETWEEN VAPOR-PRESSURE LOWERING AND BOILING-POINT ELEVATION

From the definition of the boiling point, it is readily seen that, should the vapor pressure of the boiling solvent be lowered by the addition of a solute it will cease boiling until equilibrium is again established and the vapor pressure is raised to the same value it had before the solute was added. An increase in vapor pressure will be accompanied by a proportionate increase in the temperature or

$$\frac{dp_0}{dt_0}=\frac{p_0-p}{T-T_0} \tag{118}$$

or

$$T-T_0=p_0-p\div\frac{dp_0}{dt_0}, \tag{119}$$

in which $T-T_0$ is the elevation of the boiling point of the liquid which takes place in reestablishing equilibrium between the vapor pressure of the liquid and the surrounding atmosphere, and dp_0/dt_0 is the rate of change of vapor pressure of the solvent with change in temperature.

5. RELATIONSHIP BETWEEN BOILING-POINT ELEVATION AND CONCENTRATION OF SOLUTE

Substituting in eq 118 the value of p_0-p from eq 117, we have

$$T-T_0=\Delta T=p_0x\div\frac{dp_0}{dt_0} \tag{120}$$

or

$$\Delta T=B_0x=B_0\frac{N}{N_0+N}, \tag{121}$$

in which B_0 is the boiling-point constant and represents the relation existing between the vapor pressure of the solvent and the rate of change in vapor pressure of the solvent with temperature. $T-T_0$ or ΔT is the boiling-point elevation at an atmospheric pressure corresponding to T_0.

This equation is satisfactory for dilute solutions and is useful in determining the molecular weight of various substances. At high concentrations, however, the equation does not hold, because it does not correct for the mutual attraction between the solute and solvent molecules; therefore the relationship existing between the boiling-point elevation and the concentration must be determined experimentally for each substance.

6. RELATIONSHIP BETWEEN BOILING-POINT ELEVATION AND ATMOSPHERIC PRESSURE

The boiling-point constant at any atmospheric pressure may be determined from the approximate Clausius—Clapeyron equation

$$\frac{p_0}{\frac{dp_0}{dT_0}}=\frac{RT_0^2}{\Delta H_0}=B_0, \tag{122}$$

in which R is the universal gas constant and ΔH_0 the molal heat of vaporization of the solvent at its boiling point, T_0.

If eq 122 is substituted for its value in eq 121, we have

$$\Delta T=\frac{RT_0^2}{\Delta H_0}x, \tag{123}$$

which is the boiling-point elevation equation for concentration x. If this equation holds for any atmospheric pressure at which the boiling point of the solvent is T_0, then it is true for the pressure of 760 mm Hg. When we change the subscripts of the factors in eq 123 to correspond to these pressure conditions, we have

$$\Delta T_{760}=\frac{RT_{760}^2}{\Delta H_{760}}x \tag{124}$$

and

$$\Delta T_p=\frac{RT_p^2}{\Delta H_p}x \tag{125}$$

Dividing eq 125 by eq 124, we have

$$\frac{\Delta T_p}{\Delta T_{760}}=\left(\frac{T_p}{T_{760}}\right)^2\frac{\Delta H_{760}}{\Delta H_p}. \tag{126}$$

Inasmuch as $\Delta H_{760}/\Delta H_p$ is the ratio of the molal heats of vaporization of the solvent under two pressure conditions, their values may be expressed in any unit, and we may rearrange eq 126 and write it as

$$\Delta T_p=\Delta T_{760}\left(\frac{T_p}{T_{760}}\right)^2\frac{L_{760}}{L_p}, \tag{127}$$

where ΔT_p is the boiling-point elevation at any pressure, p, at which the solvent boils at a temperature of T_p, and L_p is the latent heat of vaporization of the solvent at this temperature. ΔT_{760} is the boiling-point elevation at a pressure of 760 mm Hg, in which case the solvent boils at a temperature of T_{760}, which, for water, is equal to 373.16° K, and L_{760} is the latent heat of vaporization of the solvent at this temperature expressed in the same units as L_p. This equation, which is sometimes referred to as Tishchenko's equation [5], may be used to determine the boiling-point elevation at pressures other than that for which the values have been experimentally determined.

7. DERIVATION OF BOILING-POINT ELEVATION TABLE

As has been stated elsewhere, empirical equations were calculated from Spengler's observed data. These equations were developed in the following manner:

Inasmuch as no observations were made at a pressure of exactly 1 atmosphere, the first step was to adjust the values determined at the pressure nearest 1 atmosphere for each concentration and purity to the value it would have at exactly 1 atmosphere. This was done by means of eq 127 expressed in the form

$$\Delta t_{760}=\Delta t_p\left(\frac{T_{760}}{T_p}\right)^2\frac{L_p}{L_{760}}, \tag{128}$$

in which L_p/L_{760} was determined for each observed temperature by the equation

$$\frac{L_p}{L_{760}}=1.1074-1024t\times10^{-6}-5t^3\times10^{-9}, \tag{129}$$

where t is the temperature in degrees centigrade corresponding to the observed temperature, T_p, which is expressed in degrees Kelvin, or

$$t=T_p-273.16. \tag{130}$$

Values given by eq 129 in the range 60° to 130° C are in agreement with values of L, according to Osborne, Stimson, and Ginnings [6].

The use of eq 128 to adjust the observed values of the boiling-point elevation to the boiling-point elevation which the solution would have at 1 atmosphere resulted in a very small change from the observed values. In all cases this change was less than 0.10° C.

These adjusted values were fitted to four empirical equations, one for each purity reported, by the method of least squares. They have the form

$$\log_{10}\Delta T_{760}=aX^3+bX^2+cX+d,$$

where ΔT_{760} is the boiling-point elevation of the solution at 1 atmosphere; X is the concentration of solids in solution, in percent (Brix); and a, b, c, and d are constants from the least-squares data. The equations on page 366 show the values of the constants for each of the four equations.

Boiling-point elevations at other pressures were calculated from the values found by these empirical equations by means of eq 127. The values so calculated deviate from the observed values by a lesser amount than they do from the graphic-method values.

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XXIV. CANDY TESTS

1. INTRODUCTION

(a) GENERAL

The need of a standard or reference procedure as a starting point for a rational development of various types of candy tests has been felt for some time. The method outlined below for simple barley-sugar tests, as well as the special equipment specified for carrying it out, has been developed at this Bureau, not only as a basic procedure but also as a standard procedure for the routine testing of commercial sucrose with respect to heat stability. It is founded upon an old procedure,[20] which generally is attributed [2, 4, 5, 7, 9] to S. C. Hooker, whose directions, as transmitted to various laboratories under his supervision [21] were stated in approximately the following words.

(b) HOOKER TEST

Half a pound (227 g) of sugar is placed in a copper casserole of the following dimensions, 4 9/16 inches diameter at the top, 2¼ inches diameter at the bottom, and height 2 9/16 inches (inside measurements). After the addition of 3 oz (89 cc)[22] of distilled water, the casserole is placed over the naked flame of a burner. The flame should be regulated previously to such a size that the total time of heating required to bring the temperature to 350° F (177° C) is 21 to 25 minutes. (It has been found that this condition will be fulfilled if 200 cc of water at room temperature is brought to a point of vigorous boiling in 4½ to 5 minutes.)

[20] The procedure was described in 1897 by Wiechmann [1], not as a control test but as a method of preparing "amorphous sugar" to be used in a study of allotropy in sucrose. The two sections of the description, separated in his paper, cover roughly every point of the Hooker procedure almost word for word. The paper includes analytical data on a dozen different candy plaques, one of which had been stored under a bell jar with calcium chloride desiccant while it developed a crystallizing area, of which there is presented a record of the rate of growth to a diameter of 51 mm and an excellent photograph at this stage.

[21] Hooker's directions are quoted here, because no exact statement of them is known to be readily available elsewhere.

[22] In certain copies of Hooker's directions, which probably were intended for use with wet-packed confectioners' sugars, the quantity of water was stated as "87 cc."

The contents of the casserole are continuously stirred until the sugar has dissolved, and the stirring rod is removed. If the size of the flame has been properly adjusted the solution should start to boil in about 5 minutes after being first put over the flame. At this point an inverted watch glass is placed over the casserole; otherwise the sugar will be apt to crystallize as the evaporation proceeds.

After the heating has continued precisely 15 minutes from the time when the casserole was first placed over the flame, the watch glass is removed and the solution is then thoroughly and constantly stirred without a moment's interruption until the boiling point has reached exactly 350° F (177° C), the thermometer being used as a stirring rod. The casserole is than *instantly* removed from the flame and its contents are as rapidly as possible emptied upon a polished copper slab 14x14x¼ inches in size. In a few minutes the candy becomes brittle and can be broken up for any tests it is desired to make.[23]

The Hooker procedure is deficient chiefly in reproducibility. Experiments conducted at this Bureau indicate that most of this variability can be eliminated through the use of more definite specifica-

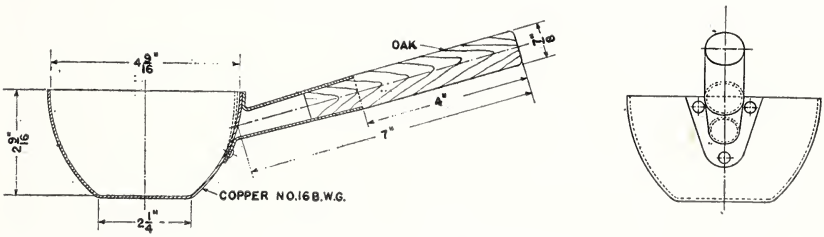

FIGURE 89.—*Copper casserole as used in Hooker's procedure.*

The drawing is adapted from the illustration presented by Murphy [5].

tions for the apparatus and procedure and by the omission of hand-stirring of the boiling sirup [4]. As a result of this study, a method has been developed which is designated the "National Bureau of Standards simple barley sugar test."

2. NATIONAL BUREAU OF STANDARDS METHOD FOR BARLEY SUGAR

The Bureau method varies from the Hooker procedure in several respects, as summarized later in this discussion. All of these modifications are important to the convenience and uniformity of the test procedure, as also to the precision and reliability of the results, especially as obtained by different operators, and particularly as obtained in different laboratories. The following is the improved procedure.

[23] Most candy and sugar technologists regard commercial sucrose as being the "weaker" the greater the degree of hydrolysis which it undergoes upon conversion into hard candy under standardized conditions [2, 4, 5, 9, 10, 11]. Hooker's procedure originally was intended to indicate, through direct polarization of the resulting candy project, the relative "strength" of any lot of sugar, conceived as the apparent resistance of the sugar to hydrolysis under such conditions. In Hooker's laboratory no other tests of the candy product were made. In later development of candy test methods, various other observations have been applied to the candy product as criteria of the quality of the sugar. When Osborn [2], in 1912, introduced candy test methods as a means of control of quality in beet sugar production, substituting porcelain casseroles for those of copper, he immediately gave heed to the rates of crystallization of the individual candy products and also devoted special attention to the color of the candy and to the tendency of the sirupy mixture to "foam" upon first coming to a boil in the candy test. He finally omitted the direct polarization in most cases. Empirical means of roughly estimating in quantitative form, the tendencies of the sugar to cause foaming and caramelization were developed somewhat later by Proffitt [4].

(a) PROCEDURE

1. Weigh 250.00 ±0.05 g of the sugar sample on a dry basis and make up to a weight of 350.00 ±0.05 g with cold equilibrium water [24] in a 600-ml chemical-resistant glass beaker (provided with a thermometer clasp, as specified on p. 375) previously tared with the thermometer and the notched watch-glass cover.

2. With the thermometer used as a stirring rod, loosen the compacted crystals from the bottom of the beaker, and mix them evenly with the liquid to form a homogeneous suspension. Continue the stirring until the crystals easily remain in suspension for some time, or until the temperature has ceased falling.

3. Replace the thermometer in its clasp (to avoid injury of the thermometer and the dripping of sirup), and set the beaker upon its supports in the stove with the burner alight and with the flame in correct stable adjusment. Immediately resume stirring of the mixture with the thermometer to prevent settling of the undissolved crystals.

4. On the instant the starting temperature of 30° C (86° F) is indicated, note "zero time" in the heating cycle (as for example, by the starting of a stop watch or a second counter).[25] Proceed with the stirring until a temperature of 70° C (158° F) is indicated, when crystals of fine or medium granulated sugar ordinarily should be practically all dissolved.[26] Clasp the thermometer at its proper working level, which will bring the bottom of the bulb to the position indicated in the drawing (fig. 90). Immediately cover the beaker with the watch glass as indicated in the drawing. Observe the sirup closely as the boiling point is approached[27] for its behavior during the transition interval between quiescent heat absorption and steady boiling is an important criterion of the probable stability of the sugar in storage as well as in candy making. There should be no considerable increase in the apparent volume of the sirup, not more than a trace of foamy scum should collect on the surface, and the transition interval should last not more than 30 seconds.[28] Steady boiling usually is barely established when the thermometer indicates a temperature about 6° C (11° F) higher than it would indicate in boiling water in the same beaker. This is assumed to be the initial boiling temperature of the sirup.

5. Allow the sirup to boil under cover until its indicated temperature is just 120° C (248° F) [4] (which in a 23-minute cooking interval occurs approximately 15 minutes after the start of heating). On the instant this temperature is indicated, lift the watch glass at one edge and tip it to drain most of the adhering condensate down the side of the beaker into the boiling sirup. Do not disturb the sirup in any other manner. Place the wet watch glass into a drying oven at a temperature of about 105° C (221° F) without washing, for it may retain a small amount of sirup.

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[24] Equilibrium water is defined on p. 271.

[25] If temperature-gradient data are desired, record elapsed time against a previously prepared schedule of temperatures. Such gradients are a valuable means of interpreting results in certain cases.

[26] If grains still can be felt with the thermometer or can be seen, remove the beaker from the stove and proceed with the stirring without further heating until the refractory grains have disappeared. Return the beaker to the stove, and stir the sirup again until the temperature of 70° C is regained. Do not include the time consumed in these operations in the recorded duration of the cooking interval.

[27] Remove the watch glass during the transition interval only if dew formation on the undersurface interferes with observation, or if its removal is required for the measurement or the quelling of foam. (See b (1), p. 373).

[28] If a layer of sudsy foam accumulates on the surface of the sirup, proceed as indicated under b (1), p 373.

6. On the instant a temperature of precisely 176.7° C (350° F) is indicated, remove the beaker from the stove, simultaneously noting the time (as by the stopping of the timer device), and dump its contents all at once onto the center of the cooling slab. This operation should be performed in such a manner as to form a nearly circular plaque. When the stream breaks, turn the beaker to an angle of about 45° and allow the sirup to drain into the center of the plaque for 10 ±2 seconds. Lift the beaker with a turn which brings the threads of sirup into its mouth, and set it upon a quenching sheet of ¼-inch aluminum or copper to prevent charring of the adhering sirup in the bottom of the beaker. Cover the beaker with the dried watch glass now taken from the oven and, when cooled to room temperature, weigh the whole assembly.

7. Five minutes after the pouring of the candy, strip the plaque from the water-cooled slab and place it in a desiccator or dry-air closet until it has cooled to room temperature. When the plaque is cool, proceed as indicated under b (2), below.

(b) OBSERVATIONS FOR THE INTERPRETATION OF RESULTS

(1) Foam Number.—When a layer of sudsy foam accumulates upon the surface of the sirup as it approaches the transition interval, the apparent volume of the mixture probably will expand suddenly at initial boiling [2, 4]. To obtain a roughly quantitative statement of the phenomenon, proceed as follows:

Observe the number of seconds elapsing from the instant the rapid expansion begins until the moment the foam subsides to its minimum volume, and record the result as "duration of foaming." Observe also the distance in centimeters from the surface level of the quiescent, nonfoaming sirup to the highest level reached by the general surface of the foam on expansion, convert the result to percentage of increase in volume, and record the number as the "volume of foam." The product of these two numbers is the "foam number" [4, 6].

Space is available in the beakers for the accommodation of but little more than a doubling of the apparent volume of the sirup with the specified size of sample. If the expansion much exceeds this value, at the standard rate of heating, it may result in the overflowing and loss of a portion of the sirup, with consequent fouling of the stove and burner. If this misfortune threatens, reduce the rate of heating; do not disturb the flame but hold the vessel by hand at a greater distance above the flame, or hold it intermittently over the flame until all danger of loss is past. Do not include any prolongation of the heating which is involved in the quelling of foam as a part of the cooking interval.

(2) Examination of the Plaque.—Notice the general appearance of the candy, especially with respect to color, transparency, inclusion of bubbles and specks, etc., and state the results in qualitative form.

Weight of the plaque.—When the plaque has cooled to room temperature, weigh it with a precision of ±0.05 g.

Projected area of the plaque.—Measure the projected area of the plaque, preferably by following the periphery of the disk itself with the stylus of a planimeter specially designed for such purposes. If this means is not feasible, first trace the outline of the plaque upon paper and later measure the area enclosed by the tracing. Express the results in square centimeters.

Slump or specific area of the plaque.—Divide the number representing the projected area by the number of grams in the weight of the plaque, and record the quotient as the "slump", or specific area, expressed as square centimeters per gram. The numerical value of this quotient, under uniform conditions of testing, increases with increasing weakness of the sugar [13].

Mean thickness of the plaque.—Measure the thickness of the plaque at a minimum of 20 random points distributed evenly over the plaque, preferably by means of a dial-type thickness gage. In lieu of this, pieces of the plaque may be measured with an ordinary micrometer. The plaque is thicker the stronger the sugar from which it was prepared (with uniform conditions of testing) [13].

Color measurement of the solid candy.—Estimate the transmission of light of 560 mμ wave length (or of three or more wave lengths, if preferred) at several clear points on the plaque or at clear points on several pieces. Compute the transmissions for layers of exactly 5 mm thickness. To minimize surface reflections, observe the pieces while freshly immersed in a water-clear, slightly supersaturated sirup of pure sucrose contained in a wide, open-top colorimeter cell of about 1-cm length (on the optical axis). Employ any suitable instrument (chap. XIX), and correct the results for any perceptible absorption of light by the immersion sirup [13].

Yield and overweight of the candy.—The total yield, y, of the candy is the sum of the weight of the plaque and the weight of the candy adhering to the boiling-vessel, thermometer, and cover. The "overweight" in grams is the difference expressed by (y—wt of dry substance introduced), which, in all standard tests, is (y—250). It represents approximately the weight of the residual water retained by the candy, partly combined as water of hydrolysis, partly as solvent or solute in the supercooled solution. In standard tests it is expressed as a percentage of the sample weight simply by multiplying by the factor 0.4.

Breaking of the plaque.—The relative brittleness or toughness of the plaque can be estimated by breaking the plaque with a suitable impact device. Ordinarily, it is simply broken by hand. In either case, the pieces are placed promptly in a container, such as a glass-top mason jar which can be closed to protect the candy from the moisture of the atmosphere. If the candy is to be examined in aqueous solution, the container should be tared.

(3) Examination of the Candy in Aqueous Solution.—From the net weight, w, of the candy stored in the container, and the yield of the candy per gram of the dry substance introduced, compute the weight of dry substance introduced (see above) equivalent to the contents of the container, as sw/y, where s represents the weight of dry substance in the sample (250.00 g in all standard tests). Add equilibrium water until the total weight of the contents is precisely double this quantity, i. e., $2sw/y$. Cover the container securely and without the application of any heat, shake or rotate it, preferably by mechanical means, until the candy is completely dissolved. Use this stock solution for whatever tests or analyses are to be made on the aqueous solutions, keeping in mind the fact that 1 g of the original dry substance of the sample is represented by 2 g of the stock solution.

(c) APPARATUS

(1) Boiling-Vessels.—Glass beakers, Griffin form, 600-ml capacity, of chemical resistant, low-expansion Pyrex or equal glass must be used as the boiling-vessels. Each beaker is to be provided with a notched watch-glass cover and with a quickly detachable combination handle and thermometer support with quick-opening spring-actuated clasp, as indicated in figure 90. For lightness and cleanliness, the handle and thermometer support are constructed mainly of aluminum. For uniformity of results, the thermometer bulb should be located precisely as indicated in the drawing, and the burner should be of precisely the form and arrangement indicated in figure 92. Since

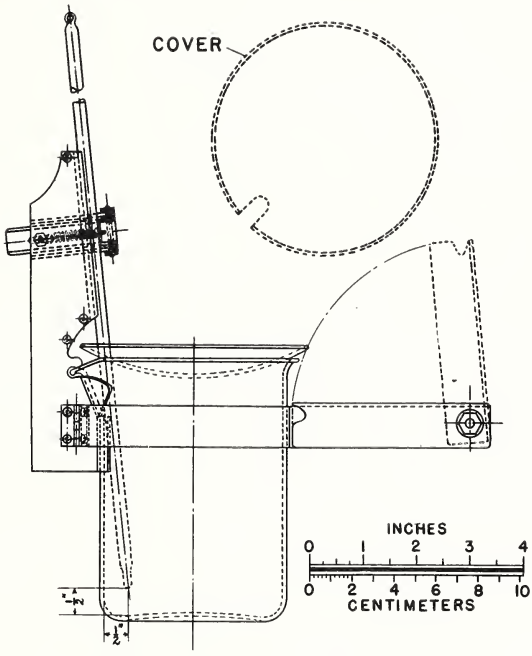

Figure 90.—*Boiling-vessel assembly.*

Consists of 600-ml chemical-resistant-glass beaker provided with a notched water-glass cover, thermometer, and handle set carrying the thermometer support with spring-actuated clasp. The aluminum handle set is clamped onto the beaker by means of the hinged hoop bands which are secured by closing the handle shell, jackknifewise, over the straight protruding ends of the bands. It is retained at a fixed level on the beaker by the V-shaped wings which bear upon the sides of the lip of the beaker, and by the short hook which rests in the notch of the lip.

variations in the thickness of the beaker bottoms cause relatively large variations in the duration of the cooking interval with any given adjustment of the burner and gas supply, beakers which are to be used interchangeably on a particular adjustment of the heating equipment should be carefully matched as to weight and as to heat transmission. A counterpoise, preferably adjustable, should be provided for the taring of each assembly. Since the handle sets are so easily removed, and should be removed while the glass parts are being washed, all weighings may be made without the handle sets. Thus consecutive tests can be run without loss of time by providing a sufficient number of matched beakers and thermometers with but two handle sets.

(2) Heating Devices.

Standard device with flow manostat for gas heating.—This apparatus, which will be described in greater detail elsewhere, practically meters the gas to the burner jets at a steady rate of flow. The heat capacity of the burner and the associated parts is small; only a few minutes of operation is required to establish a state of steady output of heat to the boiling-vessel, provided that the calorific value of the gas is approximately constant. The apparatus is comprised of the following parts:

Flow manostat.—The essential feature of the manostat, figure 91, is the balanced valve, V which floats in the orifices of the plates, OP, and is actuated by the float, F, which in turn is operated by changes in

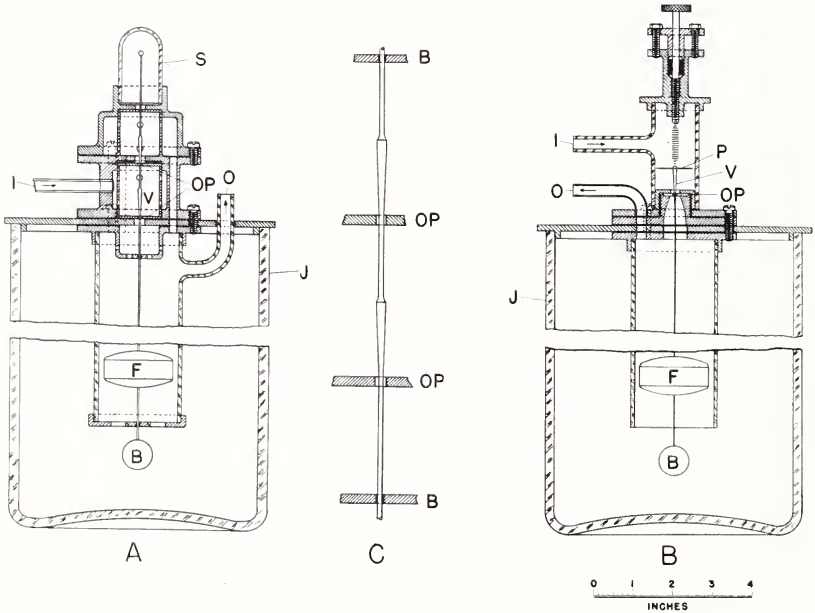

Figure 91.—*Flow manostat for gas pressure regulation.*

The preferred form, as illustrated at *A*, has a double self-balancing valve which floats freely in the two gas orifices and does not close the openings completely at any level, as illustrated more clearly in the enlarged view *C*. A simpler form of regulator with a single, spring-balanced valve is illustrated in view *B*.

the level of the hydrostatic liquid in response to changes in the pressure of the regulated gas stream. The floating valve is retained in the centered position in the orifices of the plates OP by the bearing plates B (as lettered in the enlarged view, C). The valve-and-float assembly is further stabilized by the ballast weight, B (refer to views A and B). The liquid tank J, the float chamber with the gas outlet O and the top closure S, may be made of glass, as indicated, for the convenience of visibility of the moving parts during the adjustment and operation of the manostat. However, a simpler construction has proved amply satisfactory in service. The pointer, P, (view B) is convenient with either the single or the double valve [13].

Gas from the service pipe enters at I, and the regulated gas streams for two or three burners is taken off at O. Since the regulation of pressure is dependent in part upon a steady outflow at O, which is to

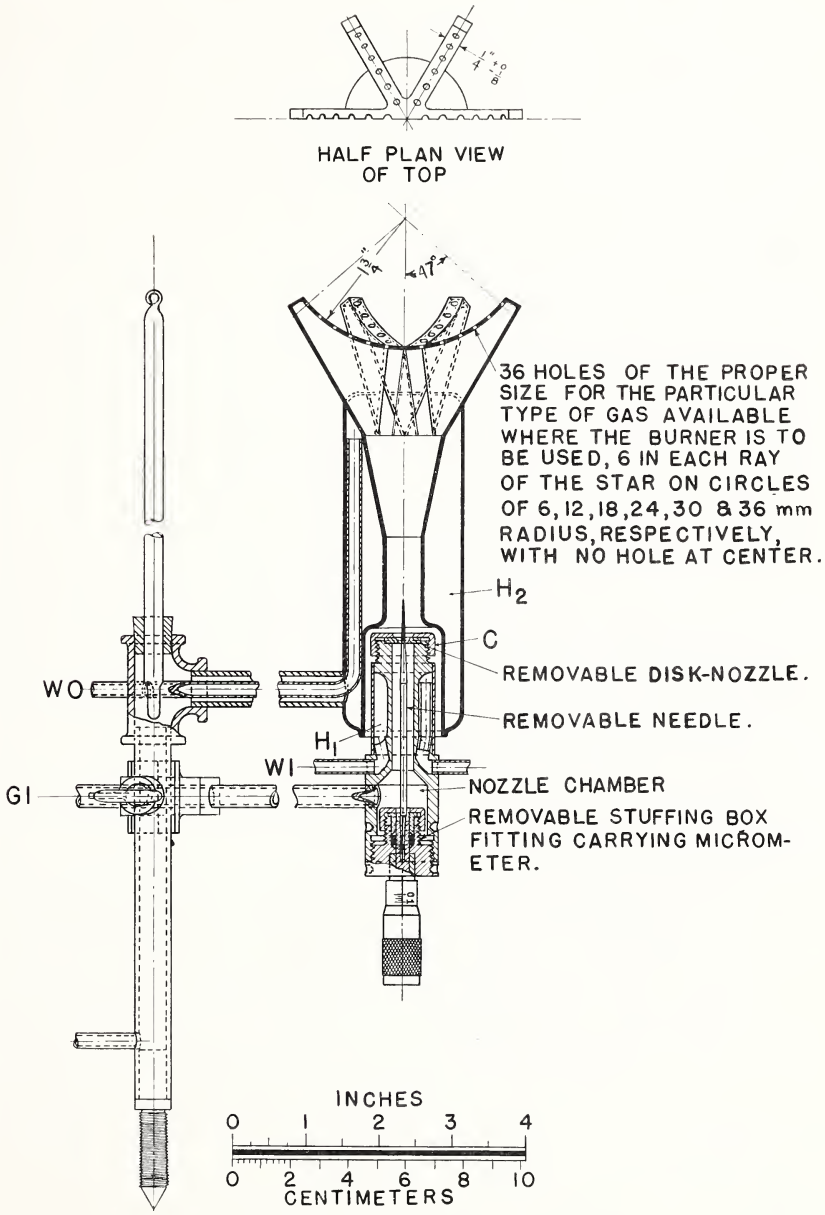

FIGURE 92.—*Special star burner.*

Vertical section, indicating the preferred form as constructed with water jackets and with a micrometer-actuated needle valve which is readily removable for operation of the unit as a simple disk-nozzle injector. The needle rests in a tapered socket in the micrometer spindle.

say, a steady consumption of gas by the burners, it follows that no change can be made in the number of burners without altering either their average individual output or else the adjustment of the regulator.

Special star burners.—The essential feature of the form of gas burner which is to be used with glass beakers (but also is suitable for use with other types of boiling-vessel) is the arrangement of the multiple-flame jets upon the curved upper surfaces of the six rays, as indicated in the drawings, figures 92 and 93. Desirable but not indispensable features are, first, the unobstructed knife-edged disk nozzle for the injection of the gas into the mixing chamber, which

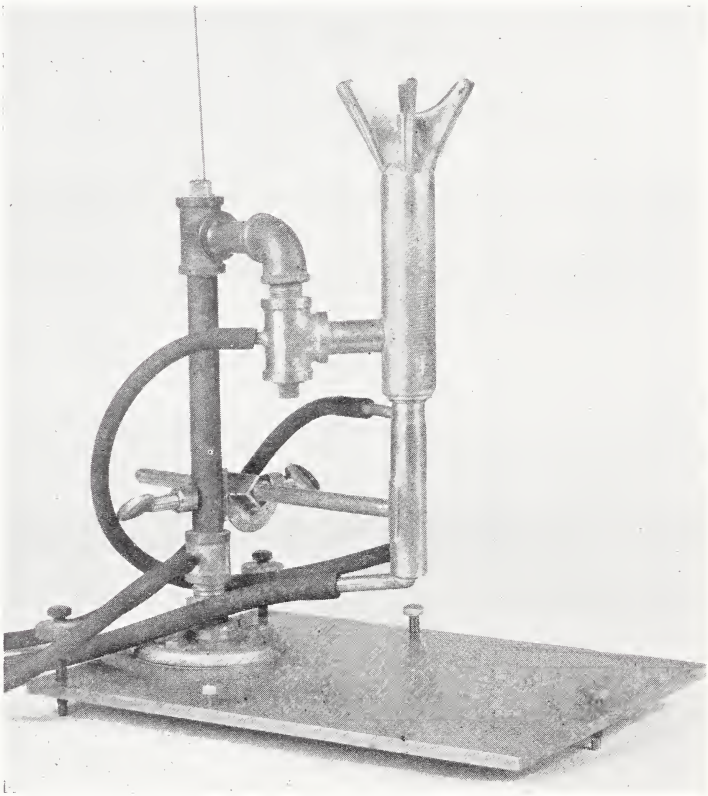

FIGURE 93.—*Special star burner as constructed with water jackets and disk nozzle, but without micrometer and needle valve.*

is readily removable for cleaning or exchange: and second, the water-cooling of the nozzle chamber and nozzle and the mixing chamber. [13]

The disk nozzles are to be properly formed of corrosion-resistant material, such as monel metal or stainless steel. A number of interchangeable nozzles with assorted diameters of orifice should be provided to facilitate adjustment of the burner output. For a given rate of discharge, the orifice of a thin disk nozzle presents maximum clearance for the flow of gas and minimum probability of clearance contraction through accumulation of dirt, tar, or polymerization waxes. Hence the disk nozzle provides stability and reliability of heat out-

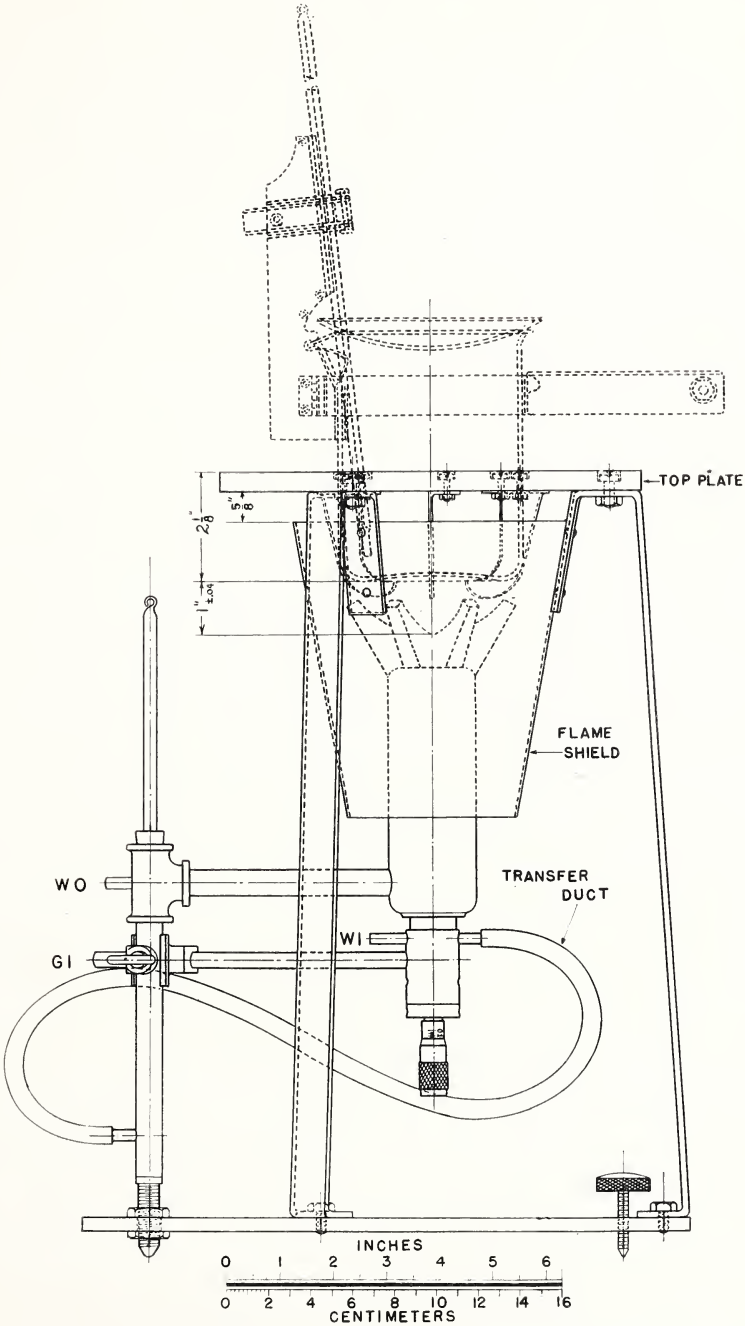

FIGURE 94.—*Stove assembly with the burner arrangement illustrated in Figure 4.*

To indicate the correct relations among the beaker, burner, and top plate, the operating position of the boiling-vessel assembly is illustrated in broken outline. *WI* represents the water inlet, *WO* the water outlet, and *GI* the gas inlet.

put by the burner. At some sacrifice of these features, but at little sacrifice of accessibility for cleaning when deposits appear, provision can be made for adjustment of the output capacity of a burner with disk nozzle by installing in the nozzle chamber a long-taper needle valve with a maximum thrust diameter somewhat less than the

FIGURE 95.—*Stove assembly with the burner arrangement illustrated in Figure 5.*

The boiling-vessel assembly is in position for the carrying out of a candy test.

diameter of the orifice, which it is arranged to penetrate concentrically. The arrangement is indicated in figure 92.

In figures 92 and 94 the nozzle chamber into which the gas inlet, *GI*, leads is enveloped by its water jacket, H_1, through which the current of water passes from its inlet, *WI*, to the transfer duct leading to the mixing-chamber water jacket, H_2, whence it flows to waste through the outlet, *WO*. By means of the vertical adjustment provided for the nozzle chamber assembly, the cap, *C*, can be brought to

act as a shutter against the mouth of the venturi of the mixing chamber to control the uptake of primary air. Thus an annular inlet, open at the bottom, is formed for the primary air between the jacket of the nozzle chamber and the skirt of the mixing chamber.

Stoves, or support assemblies.—The functions of the stove, figures 94 and 95, are to support the boiling vessel and burner in constant locations and thus maintain the correct spatial relations between them; to shield the flames and hot combustion gases from the disturbances caused by cross drafts (provided they are not too strong) and otherwise to assist in directing the hot gases against the bottom and sides of the vessel below the surface level of the solution; and finally, to divert the hot gases away from the sides of the vessel above the solution.

The top plate, of transite board with centrally located hole into which the beaker fits, is supported on three strap-iron legs which also support the truncated conical flame shield of polished sheet aluminum. The lower ends of the legs are bolted to the wide iron base upon which the burner is mounted, which in turn is supported upon one fixed foot and two leveling screws.

In stoves for use with glass beakers, which for any particular nominal size vary slightly in diameter, the central hole is cylindrical and just large enough to avoid any binding when the largest beaker in the set is inserted. The beakers are supported at the correct height above the burner (and at the correct insertion through the plate) by means of three thin Monel metal or stainless steel brackets attached to the under side of the plate. The boiling-vessel assembly should be set into the stove with the center of the thermometer bulb in a vertical plane bisecting the angle between two adjacent rays of the burner.

Inclined manometers (or gages).—For the convenient observation of the service pressure and the regulated pressure of the gas in the making and inspection of the adjustment of the flow manostat and burners, provide a pair of oil- or water-filled hydrostatic gages with scales about 100 cm long and inclined at suitable (and therefore different) angles.

Other types of heating equipment.—Electric-resistance heaters, for example, may be used in place of the special star burner with flow manostatic control described above, provided ample comparative candy tests on samples of a sufficient range of quality have demonstrated that they yield results equivalent to the results obtained with the burner.

Adjustment of the heating device.—The heating device is adjusted in the following manner: A minimum of four standard simple barley-sugar tests (basic method, p. 372) are run on a pure sucrose sample (p. 385), and the heating device is so adjusted that the mean duration of the time of cooking, between the temperatures 30° and 176.7° C, shall be 20 minutes ±20 seconds. Make similar tests at sufficiently frequent intervals to assure that adjustment is not changing.

The first (or coarse) adjustment is made by installing the proper disk nozzle in the burner. The nozzle is of such a size as to yield nearly the required interval. Final adjustment is made by changing the level of hydrostatic liquid in the flow manostat. As a preliminary criterion of adjustment, it is convenient to heat 300.0 g of water in the

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600-ml beaker through the 50-degree interval from 30° to 80° C (or the 90-degree interval from 86° to 176° F). The cooking interval will be approximately six times the time required to heat the water through the specified interval, i. e., the water should heat in approximately 3 minutes 20 seconds as the mean of a minimum of four tests.

(3) THERMOMETERS.—Mercury-in-glass thermometers are suitable for all ordinary candy-test procedures, provided the instruments are properly constructed. They may be graduated in either the centigrade or the Fahrenheit scale, as specified by the user, but must not be graduated in both scales on the same thermometer. They should conform preferably with the specifications presented below, which provide an instrument of low lag. Alternatively, thermometers conforming with ASTM Specifications D 183–25 or thermometers for general use may be employed.

SPECIFICATIONS FOR CANDY-TEST THERMOMETERS

TYPE.—Etched stem, glass.

LIQUID.—Mercury.

RANGE AND SUBDIVISION.—Minus 10° to plus 200° C, in 1.0°, with expansion chamber at the top to permit heating to 50° above the upper limit of the scale, or plus 14° to 390° F, in 2.0°, with expansion chamber at the top to permit heating to 90° above the upper limit of the scale.

TOTAL LENGTH.—340 to 360 mm.

STEM.—Plain front, enamel back, made of suitable thermometer tubing. Diameter 6 to 7 mm.

BULB.—Corning normal or equally suitable thermometric glass. Diameter not less than 4 mm and not greater than 5 mm. Length not less than 10 mm and not greater than 15 mm.

DISTANCE FROM BOTTOM OF BULB TO −10° C OR 14° F MARK.—80 to 100 mm.

DISTANCE FROM 200° C OR 390° F MARK TO TOP OF THERMOMETER.—30 to 70 mm.

LENGTH OF UNCHANGED CAPILLARY between top of bulb and first graduation mark, 60-mm minimum; and between the last graduation mark and the expansion chamber at the top, 10-mm minimum.

TOP FINISH.—Glass ring.

SPACE ABOVE MERCURY.—Filled with nitrogen or other suitable gas.

GRADUATION.—All lines, figures and letters are to be clear cut and distinct. Maximum width of graduation lines, 0.1 mm. On the centigrade scale, all graduation lines at multiples of 5° are to be longer than the remaining graduation marks. Graduations are to be numbered at each multiple of 10°. On the Fahrenheit scale, all graduation lines at multiples of 10° are to be longer than the remaining graduation marks. Graduations are to be numbered at intervals of 20° beginning at 20°.

IMMERSION, 76 mm.—The words "76-mm immersion" and a line around the stem at a distance of 75 to 77 mm above the bottom of the bulb are to be etched on the stem.

SPECIAL MARKING.—The words "NBS CANDY TEST", a serial number and the manufacturer's name or trade-mark shall be etched upon the stem. The marking "°C" or "°F", as the case may be, shall be etched on the front of the stem above the scale.

SCALE ERROR.—The error at any point on the scale, when the thermometer is standardized at 76-mm immersion in a room at 25° C temperature, shall not exceed 1° C or 2° F.

CASE.—The thermometer shall be supplied in a suitable case, on which shall appear the marking "NBS CANDY TEST, −10° TO 200° C" or "NBS CANDY TEST, 14° TO 390° F", as the description may require.

NOTE.—For the purpose of interpreting these specifications, the following definitions apply:

The total length is the over-all length of the instrument, as supplied.

The diameter is that measured with a ring gage.

The length of the bulb is the distance from the bottom of the bulb to the beginning of the enamel backing.

The top of the thermometer is the top of the finished instrument.

(4) Cooling Slabs.

Water-cooled slabs for standard plaques.

As constructed according to the drawing, figure 96, two circular plates of aluminum are drawn down at their peripheries to form short skirts which can be placed edge to edge to form the water chamber. These are notched in such a way that when so placed, a pair of circular openings can be formed for the insertion of the inlet and outlet nipples. Within the chamber, with its inlet nipple protruding through one of the openings, is placed a flat spiral coil of aluminum tubing in contact with both plates and having its open discharge end at the center of the assembly. The outlet nipple is inserted in the other hole. The coil is tack- or spot-welded to one of the plates at a sufficient number of points to assure its remaining in place, and the joints between the skirts, as also between the nipples and the skirts, are carefully welded.

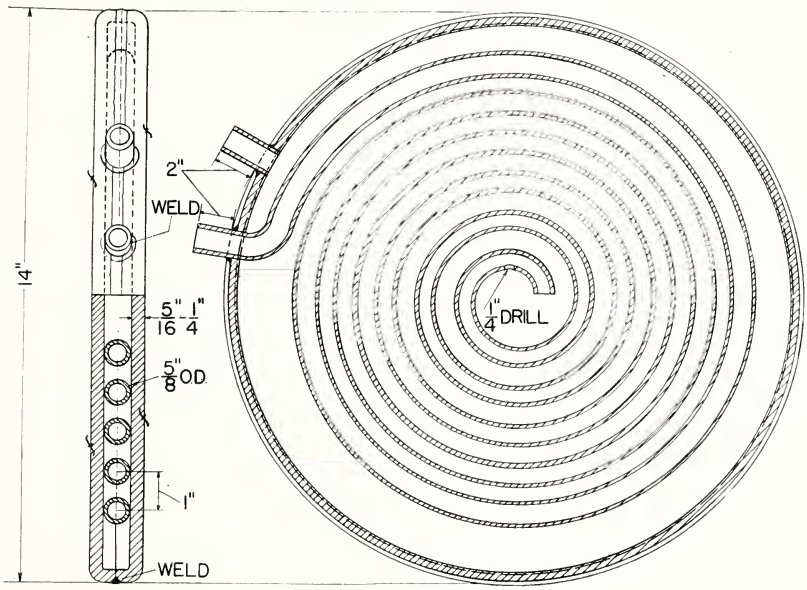

Figure 96.—*Water-cooled slab.*

Plan view and side elevation. The latter is quarter-sectioned to illustrate the construction described in the text.

The faces marked *f* are to be carefully polished and they must not be marred in use. Alternatively (but with some disadvantages), the slab may be constructed of copper, with brazing or silver soldering in place of welding.

(This slab may be constructed in any other manner which achieves approximately the same result and cools the candy evenly by a flow of water directed to absorb the heat most rapidly at the center of the plaque, where the temperature is highest.)

In service, the slab should be level. Water should enter the coil at a temperature of 25° C and should flow at a rate of about 5 liters per minute into the center of the water chamber, thence through the spiral path between contiguous turns of the coil to waste through the outlet nipple.

Quenching plate.—For the prompt cooling of the superheated bottom of the beaker (to prevent charring of the residual sirup, which fouls the glass and complicates the washing), provide a square piece of ¼-inch aluminum or sheet copper measuring 12 to 14 inches square. Aluminum is preferable to copper because of its lighter weight.

(d) HEATING CYCLE

The heating cycle of any candy sugar test includes the cooling interval (during which the material is restored to room temperature) as well as the cooking interval, which itself includes three main regimes, or phases, of heating, as indicated by the temperature gradients of the cooking interval presented in figure 97. These three phases comprise (1) The bringing of the mixture to the boiling point (accomplished under two regimes in the NBS method (2) the concentration (usually under cover) to proximate saturation at the current temperature, and (3) the further concentration of the sirup under continuously increasing supersaturation to the terminal temperature. From what is said below of the utility and reliability of the candy test, it is evident that the most advantageous duration to select for each of these intervals is that which differentiates the samples most precisely and most reliably in respect to their stability properties. The same thing is true of the terminal temperatures. If the heat effect is carried beyond an established optimum in either respect, the separation becomes blurred.

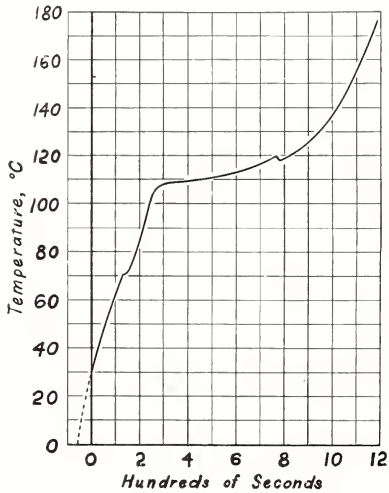

FIGURE 97.—*Temperature gradients developed during the 20-minute cooking interval of a simple barley-sugar test conducted according to National Bureau of Standards procedure, using a 600-ml glass beaker on the stove assembly illustrated in figure 7.*

Two regimes of heating prevail in the first (or preboiling) phase of this procedure. The resulting four regimes of heating: (1) with stirring of the uncovered sirup, (2) without stirring of the covered sirup prior to boiling, (3) with boiling of the sirup under cover, and (4) with boiling of the sirup in the open beaker are set off by the three abrupt flexures of the temperature curve (a) at 70° C, where stirring is terminated; (b) at the transition from quiescent heating to vigorous ebullition of the sirup; and (c) at 120° C, where the sirup is uncovered.

(1) DURATION OF THE COOKING INTERVAL.—In all standard procedures conforming with these general methods of candy testing, the correct cooking interval is assumed to be that which results when the test is conducted in apparatus which has been carefully standardized and the heating device adjusted with reference samples of pure sucrose (p. 385) in the basic simple barley-sugar test, as directed on page 372. As long as the specified adjustment of the apparatus is maintained the correct cooking interval will be yielded in any standard test on a sample of any appropriate composition, although the actual time elapsing between 30° C (86° F) and the terminal boiling temperature may be not quite the 20 minutes ±20 seconds, required under reference conditions.

From this it follows that if the mean duration of the cooking interval in a minimum of four standard simple barley-sugar tests on an

"unknown" sample of commercial sugar should deviate from the mean duration observed in calibration with the prototype sample by very much in excess of ±20 seconds, such deviation from the mean could be regarded as a characteristic property of the commercial sample.

(2) Duration of the Cooling Interval.—Although the decomposition of the ingredients of a candy test is most rapid at the terminal boiling temperature, there seems to be less promise of a gain in differentiation of samples [10, 11] by either delay or prolongation of the cooling interval than in shortening it and making it more uniform. This fact sufficiently explains the specification of the water-cooled slab in standard tests [13].

(e) SAMPLES

(1) Types of Materials Tested.—This discussion of the National Bureau of Standards improved simple barley-sugar test is limited to its use (a) in the standardization of equipment for candy tests in general, which involves only reference samples of specially purified sucrose (see below); and (b) in the routine inspection of commercial white sugars, where ordinarily only samples of char-refined sugars (and direct-consumption sugars of comparable purity) will be involved. A discussion of the modifications of the basic procedure permitted for the setting up of other types of candy tests will be presented elsewhere [13].

(2) Reference Samples.—Reference samples for the purposes of candy-test procedure include two general classes of materials: (a) Specially purified lots of an individual chemical substance, such as sucrose, which, for practical purposes, are essentially reproducible. These may be designated primary or prototype samples, (b) materials such as commercial sucrose, dextrose, and corn sirup. As a class, these may vary considerably in composition.

For the most critical reference purposes, prototype sucrose prepared according to the method of Bates and Jackson [3] is specified. For the standardization of equipment (p. 381), grade *A* char-refined sugar generally serves for the reference sample which, although specially purified as a commercial product, really belongs to the second class of reference material.

(f) IMPROVEMENTS OF THE NATIONAL BUREAU OF STANDARDS METHOD OVER THE HOOKER PROCEDURE

For the reasons stated in the introduction, the National Bureau of Standards basic method for the simple barley-sugar test differs from the Hooker candy test in the following details:

The boiling vessel is a 600-ml chemical-resistant glass beaker with detachable thermometer support in place of a copper casserole with no thermometer support.

The weight of sample is 250.00 g of sugar on a dry basis, instead of ½ pound without reference to moisture content.

The water is added to make up to a total weight of 350.00 g, i. e., 100.00 g of total water, including the moisture in the sample, instead of 3 oz (87 or 89 ml) of water by volume. This involves a decrease of about 2 percent in the ratio of sugar to water.

The cooking interval starts at a standardized initial temperature of 30° C (86° F) instead of at a haphazard room temperature.

The duration of cooking is specified for reference conditions only instead of for each individual test, and the interval is changed from what amounts to 23 minutes ±2 minutes to 20.00 minutes ±20 seconds (for the reference conditions) and to whatever interval of time results with reliably adjusted apparatus in the individual tests on the unknown samples.

The form and arrangement of the burner are definitely specified instead of being left to chance, and means are provided for attaining the precision required.

The boiling vessel is covered at the moment the temperature of the mixture reaches 70° C (158° F), with the sugar practically dissolved, before, instead of after, boiling has commenced.

The vessel is uncovered at the instant the sirup has attained a temperature of 120° C (248° F) instead of precisely 15 minutes after the heating was started [29].

Once the sugar is approximately all dissolved and a temperature of 70° C (158° F) is attained, the thermometer remains fixed in the clasp attached to the vessel throughout the remainder of the cooking interval, with its bulb located at a definite place in the sirup where it is least exposed to direct radiation from the vessel bottom immediately above the flame, and at a place where the sirup is least superheated and least subject to fluctuation of temperature. Hand stirring of the uncovered boiling sirup is omitted.[30] No stirring rod is used at any time.

The plaques are formed on a water-jacketed metallic slab which is supplied with a steady current of water at a temperature of 25° C (77° F), instead of on a simple sheet of copper which varies in temperature. This augments the uniformity of heat exposure to which the different samples are subjected.

For the observation of certain variable properties of the samples, which were not comprehended in the original Hooker candy test, the National Bureau of Standards basic method provides special means. Especially notable among these properties are the varying tendencies of the samples to foam at the initial boiling, to "froth" later, to form colored compounds in the test, and to slump or spread and yield different specific areas in the formation of the plaque.

The specifications are planned for systematic modifications in the less critical details to provide for the setting up of specialized procedures meeting the requirements of various types of candy tests not considered in the present discussion. The Hooker procedure was devised for a very limited field of service.

(g) UTILITY AND RELIABILITY OF THE CANDY TESTS

Barley-sugar tests and the associated observations offer one of the simplest and surest means of evaluating the quality of commercial

[29] This specification obviates the possibility that the sirup may become considerably supersaturated while the vessel is still covered; thus it avoids danger of starting crystallization by the shock of uncovering the vessel. Moreover, when tests are operated on different cooking intervals (for which provision will be made in specialized procedures not covered in the present discussion), they are placed on a more nearly uniform basis in respect to the effects of uncovering when uncovering occurs at a uniform temperature instead of at a uniform time from the start of heating [4].

[30] It was shown as long ago as 1913–14 that hand stirring of the boiling sirup is a productive source of variability in the results obtained by different operators of the Hooker procedure [4].

white sugars. The Hooker procedure has proved adequate for verifying the purification of the most highly refined commercial products and for detecting gross faults of purification in products of ordinary quality. Regardless of the classification of the product in trade, a lot of sugar which consistently yields excellent barley sugar in the Hooker test almost certainly will prove adequately refined for practically any manufacturing use. Conversely, a lot which repeatedly yields poor results in this test assuredly contains inexpedient quantities of impurities, either too little of certain favorable kinds or too much of the deleterious kinds. Since impurities of the latter class can impair the keeping qualities of the sugar as seriously as they affect its suitability for manufacturing uses, candy tests have a much broader field of usefulness than is comprised by the needs of the confectionery industry alone. For many years certain progressive producers of refined and direct-consumption sugars have used candy tests of various kinds as a guide to the improvement of their wares, and as a means of routine control in the daily maintenance of the particular quality standards which each producer has set for his output. All too frequently general consumers have overlooked the possibilities of the candy tests, not merely as a means of inspecting their purchases or as an instrument for comparing the different products offered, but also as a basis upon which specifications can be definitely established prior to purchase. Important disputes have arisen over the stability of sugar in storage, as well as in manufacturing operations, which might have been avoided through such specifications. Losses of sugar are suffered by producers themselves, as well as by handlers and consumers, in spoilage which could be forestalled through a more extensive use of candy tests.

In the sugar and confectionery industries, two phases of the effects of impurities upon the stability of sugar in candy tests commonly are distinguished as the inversion, or *hydrolysis*, of sucrose and the *caramelization* of the resulting mixture of sucrose, the products of hydrolysis and certain other substances which may be present. Caramelization is a phenomenon which comprises numerous complex reactions resulting in the formation of colored compounds and other substances which are deleterious to the quality of candy.[31] The types of reaction which occur, and the velocities of the reactions (hence the extent to which they progress during any individual test), are influenced by the particular regime of conditions which obtains during the operation of the test, not solely by the kinds and the amounts of impurities present. Therefore, the arbitrary schedule of heat exposure of the sample under arbitrary conditions of operation ought to be specified within sufficiently narrow limits of variability to assure that the resulting decomposition shall be practically proportional to the reciprocal of the stability of the material. The quality of the sample[32] finally is judged by an examination of the product of the test. While a visual examination of the plaque may serve the more inexact purposes

[31] Involved in both phases of the instability of the material are not only various decompositions and degradations of sucrose and the products of hydrolysis, but also reactions comprising several types of chemical synthesis, probably including reversions and polymerizations and possibly chemical combinations between glucose and amino acids or between glucose and proteins in certain instances. The reactions are so numerous and yet so generally interdependent and (with but slight alteration of conditions) so variable that their chemistry and kinetics never have been cleared up, even for a single case.

[32] Except those phases of the quality which are indicated by the appearance of the sirup while boiling. Differences of quality are distinguishable by this method in only a limited number of samples. (See "foam number", p. 373.)

of a candy test, any quantitative statement of the stability of the sample must depend upon analytical procedure and other physical measurements. Examples are the estimation of sucrose hydrolysis (as by polarimetric or copper-reduction methods), the estimation of caramelization (as by measurements of the color in the solid plaque or in a water solution of the candy), and the estimation of the "slump," or specific area, all as outlined above.

Appraisal of the *differences* in the stability of the various samples, and the separation of the samples accordingly into various classes, is practicable only to the degree that the particular candy-test procedure approximates a reliable reproduction of a constant program of operating conditions each time it is applied. This is to say that the variability among the programs established in numerous individual tests on random samples of the same lot of sugar must result in much smaller differences in decomposition (as distinguished by the chosen methods of examination) than the variations in decomposition arising from the differences in stability of the different lots of sugar that are to be separated on the basis of quality. The tolerances for deviation from a constant program must be smaller the more precise the separations are to be. On the other hand, the minimum tolerances which may be imposed are limited by the character of the candy-test procedure available.

The minimum feasible tolerances which may be stipulated for candy tests according to the Hooker procedure are so great that satisfactory separations of samples on a quality basis are impracticable. This is doubly evident where different operators are involved, what with inadequacy of directions as to arrangement of apparatus and what with the inclusion of details of procedure which inherently are subject to individual variability. No long array of samples could be arranged precisely in the order of minutely graduated differences of stability, nor could the degree of departure of a sample from an established standard of quality be indicated, on the findings of candy tests carried out by different operators by means of the Hooker procedure alone or by means of any of its ordinary modifications. The deviations are so great, indeed, that nearly every user of the test has entertained at least transient doubts that the results obtained even by a single operator are valid criteria for any useful separation of samples on a stability basis [11, 12]. The circumstances are complicated by the failure of many users to appreciate the fact that no finer separations should be demanded than definitely will be put to practical use.

Very pure sucrose in candy tests is distinctly weak but relatively stable in respect to caramelization. The purest commercial products have similar characteristics in both respects. Because of this, certain brands of "first-run" char-refined sugar, as produced for confectioners' use, have been strengthened at the refinery for many years by the addition of small quantities of sodium carbonate or sodium bicarbonate [33] to the water used for washing the crystals [5]. The small amount of impurity thus deliberately introduced has but little influence upon the color of hard candy produced from the sugar, although much excess of the alkali would bring about marked caramelization.

[33] In 1897 Wiechmann presented data [1] on experimental suppression of sucrose hydrolysis by the presence of 1 part of calcium oxide, sodium carbonate, or sodium bicarbonate, in 100,000 parts of refined cane sugar during its conversion to barley sugar. Possibly even earlier, Hooker initiated the practice of strengthening confectioners' sugars, in response to the complaints of certain consumers. The treatment was devised and originally controlled through the Hooker candy-test procedure.

The stability of refined cane sugar of ordinary quality is inferior to that of the strengthened confectioners' sugars in respect to both hydrolysis and caramelization [5]. On the other hand, beet sugars generally tend to be distinctly stronger than either type of cane sugar but definitely less stable than either as to caramelization. There are notable exceptions to these usual relations of the three types of sugar mentioned. Indeed, the stability gradations of all sorts are so nearly continuous that probably no one would propose to distinguish the types of sugar to which many individual samples belong, solely on the evidence of candy tests.

Because such gradations are continually encountered, most users and prospective users of candy tests need a method which is both more reliable and more precise than any of those heretofore available. For selecting or for segregating different lots of sugar according to the requirements of different consumers, without an excessive number of tests, a high degree of reliability is demanded of the individual candy test. For the precise control of quality in sugar production in any plant with relatively little variation of stability in its products, the candy test procedure should have a high degree of reproducibility to permit stipulation of small tolerances of standard deviation. For many other purposes, like precision must be attained. The method and equipment described for the National Bureau of Standards simple barley-sugar test procedure are designed to reduce the standard deviations, as compared with those which prevail in the candy tests heretofore available, (1) by diminishing the variations of practice through more specific directions, (2) by diminishing the influence of the operator's individual technique upon the procedure, and (3) by greatly reducing instrumental variability in several important respects. Providing these specifications are adhered to in detail both as to operation and equipment, this enhancement of precision in candy tests should be realized in fact. With attention to the order of occurrence of stability variations in relation to the usual control and operating data of a plant, as a clue to the presence or to the advent of "assignable causes", manufacturers can make use of the increased precision as a means of bringing the production of sugar more definitely within the field of statistical control as practiced in certain other industries. The dependability and increased convenience of the new procedure, once the equipment is installed, and as compared with what heretofore has been available, should place the candy test on a much surer footing from the viewpoint of the consumer as well as the producer.

3. CONCLUSION

After quoting Hooker's directions for candy-test procedure for comparison, directions for a new and greatly improved simple barley-sugar test method are presented in detail, together with specifications for the apparatus required for its use. It is proposed not only as a standard method for the inspection of commercial sucrose with respect to stability to heat, but also as a model procedure which with suitable modification can be converted to various other types of candy tests for the examination of all sorts of sugar products. Details of the latter use are reserved for discussion in another place. It is pointed out that the method as used for the examination of commercial sugar is of value both to the producer who wishes to establish a more effective

control of the quality of his product, and to the consumer who either purchases sugar on quality specifications or allocates his purchases to different uses according to their quality. The possibility has been suggested of implementing the control of quality in the production of sugar through the introduction of modern statistical methods which make use of the order of occurrence of stability variations as a clue to their assignable causes.

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XXV. PREPARATION AND PURIFICATION OF PURE SUGARS

1. DEXTROSE

With a view to assisting in the unification of methods of sugar analysis, the National Bureau of Standards issues chemically pure dextrose as one of its standard analyzed samples. This was first issued in 1914. At that time, and for some years thereafter, the method of purification and crystallization was that devised by Jackson [1]. The raw material used was the purest form of commercial dextrose obtainable at that time and was marketed under the trade name of Cerelose.[34] It was a brownish-colored granular material containing about 87.2 percent of dextrose, 3.9 percent of nonfermentable sugars, 0.55 percent of ash, and a quantity of dextrins. The method is as follows:

The impure material is submitted to a preliminary treatment similar to that described by Bauer [2]. The crude material is digested in a shaking machine with alcohol in order to wash the mother liquor from the crystals. The mass is then poured into a centrifugal machine and drained at high velocity. The drained crystals are then washed repeatedly in the rotating basket with fresh portions of alcohol. The washed substance is dissolved by heating in 40 percent of its weight of water and 140 ml of alcohol added for each 100 g of the washed substance. This mixture is then heated on a steam bath and filtered to remove the precipitated impurities. The filtrate is evaporated in

[34] At the present time this name is applied to a highly purified commercial dextrose having the physical appearance of granulated beet or cane sugar.

the vacuum boiling apparatus described on page 393 to about 60 percent of sugar. The supersaturated liquid is then transferred to a shaking machine, a few crystals of dextrose hydrate added, and the substance allowed to crystallize in motion. After standing overnight, the crystal mass is centrifuged and washed four to five times with redistilled alcohol. The crystals obtained are very white and already possess a high purity. They are then dissolved in water, the solution filtered through asbestos into the boiling apparatus, concentrated, and recrystallized from the aqueous solution. The second crystals are carefully dried and analyzed for moisture, ash, polarization, and reducing power. If these tests indicate the presence of any remaining impurity, the recrystallization is repeated until a satisfactory product is obtained.

The crystals thus obtained are dextrose hydrate. Formerly in the preparation of standard samples the hydrate was freed of its water of hydration by heating in an electric oven at 60° to 70° C.

The above method of purification was followed for some years, until there became available white crystalline dextrose in commercial quantities. The following modification of the method of purification was then adopted. A quantity of the white crystalline dextrose is dissolved in hot water to make a 60 percent solution. This is treated with char and filtered. The filtrate is concentrated in a glass boiling apparatus under reduced pressure to a sirup of about 80 percent of dextrose. The thick sirup, which is brought to a temperature of 55° C, is seeded with crystals of anhydrous dextrose and placed in a rotating crystallizer enclosed in an insulated, electrically heated cabinet held at 55° C. The crystallization is usually complete within a few hours. The temperature is reduced until the massecuite has reached the temperature of approximately 30° C, when the crystals are separated on a centrifugal machine and washed with alcohol. The crystallization is repeated until analysis shows the material to be of the requisite purity. The air-dried crystals of anhydrous dextrose, thus obtained, contain less than 0.1 percent of moisture. The material is finally dried in vacuum desiccators containing suitable drying agents, with or without the aid of heat, to a moisture content of 0.01 percent or less. This purified material is issued as Standard Sample 41, Dextrose.

In the preparation of pure dextrose hydrate the 60-percent solution, which has been treated with decolorizing carbon and filtered as described above, is seeded with crystals of dextrose hydrate and rotated in the crystallizer at room temperature until crystallization is complete. The crystals are centrifuged, washed with alcohol, and dried in the usual manner.

The standard dextrose sample may be used as a standard in methods for the determination of reducing sugars to replace the usual invert-sugar solution and has the advantages of greater convenience in the preparation of the solution and greater certainty of composition. Some uncertainty arises in the preparation of invert-sugar solutions on account of the method of inversion employed. Reversion products may be formed, or either levulose or dextrose injured by too prolonged action of the acid. Furthermore, if the solution is preserved, decomposition may occur if either acid or alkali is in excess. The standard dextrose solution may be prepared very readily and conveniently as

needed by weighing out the required amount of solid substance and dissolving in the necessary volume of water.

2. SUCROSE

Most of the methods for the purification of sucrose which have been described depend upon the use of alcohol as a precipitant. Sucrose is almost insoluble in absolute alcohol, and its solubility in alcohol-water mixtures diminishes very rapidly as the concentration of alcohol increases.

(a) METHOD OF HERZFELD [3]

Prepare a cold, saturated, filtered, refined sugar solution and with continual stirring add an equal volume of 96-percent alcohol. Filter after 15 minutes, wash with ether, and dry in a water bath.

(b) METHOD OF HERLES

This method gives particular attention to the elimination of raffinose. To exclude traces of raffinose, precipitate a cold, saturated, filtered solution of refined sugar with alcohol, warm on a water bath to 60° C, decant the solution, pour fresh alcohol on the precipitate, warm while stirring, decant again, wash the sugar on a filter with absolute alcohol, and dry in a thin layer on filter paper at 30° to 40° C.

On account of the well-known solubility of raffinose in methyl alcohol, many operators have used this as a precipitant to insure the removal of this impurity.

(c) METHOD OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS [4]

To prepare pure sugar, further purify the purest commercial sugar in the following manner: Prepare a hot, saturated, aqueous solution, precipitate the sugar with absolute ethyl alcohol, spin the sugar carefully in a small centrifugal machine, and wash in the latter with absolute alcohol. Redissolve the sugar thus obtained in water, again precipitate the saturated solution with alcohol, and wash as above. Dry the second crop of crystals between blotting paper and preserve in glass vessels for use. Determine the moisture still contained in the sugar and take this into account when weighing the sugar which is to be used.

(d) METHOD OF BATES AND JACKSON [5]

A method of purification has been developed at this Bureau in which recrystallization from aqueous solution is utilized. The purest granulated sugar of commerce is dissolved in an equal weight of water. This relatively dilute solution is clarified from albumenoids and suspended material by the addition of alumina cream which has been carefully freed from soluble salts by continued washing and testing the wash water with barium chloride. The solution of sugar is filtered by pouring on large, fluted filters of hardened filter paper. The filtered solution, which usually has the brilliancy of distilled water, is boiled in a vacuum-distilling apparatus at a temperature not exceeding 35° C until the concentration of the solution, which was initially 50 percent, reaches 76 to 80 percent.

The requisites for a serviceable concentrator may be briefly summarized as follows: (1) Cleanliness, (2) low boiling point, (3) large capacity, and (4) filtration of entering sirup.

The concentrator is shown diagrammatically in figure 98. The entire assembly, with the exception of the aluminum vessel, *B*, and condensing coils, *C*, is of glass; and with the exception of the small asbestos filter, the sirup never comes in contact with any other substance. The evacuating is done by a power-driven vacuum pump or an aspirator connected at *D*. When it is desired to concentrate a sugar sirup, the procedure is as follows: The solution, usually approximately of 50 percent concentration, is placed in the flask, *A*, and the entire system evacuated up to the cock, *E*. This cock is then carefully opened and the solution slowly driven through the asbestos filter into the boiling flask, *F*, capacity 13 liters. Here it is gently warmed by the water bath, and the temperature of the sirup noted on the thermometer, *G*. In order to obtain any desired boiling point, it

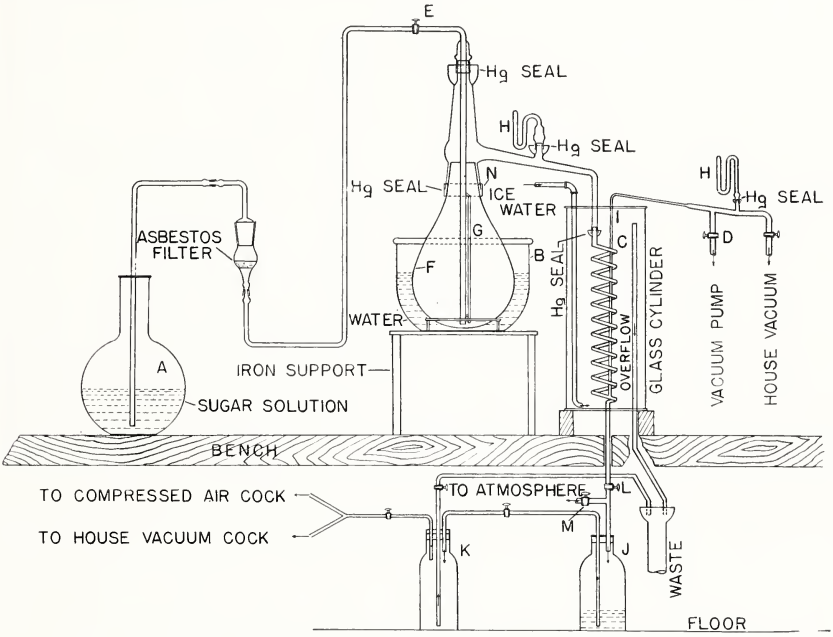

FIGURE 98.—*Apparatus for concentrating sirups in vacuum.*

is only necessary to regulate the pressure, as indicated by the mercury gages *H*, *H*. The efficiency of the assembly is such that sirup is rapidly brought to the desired concentration of about 80 percent at a temperature below 32° C. This is made possible by the high efficiency of the condensing system and by having all joints carefully ground to fit. The stopcocks are lubricated with water or sugar sirup. The condensing coils, *C*, are of copper, eight in number, connected in parallel, and immersed in ice water. To prevent vapor reaching the vaccum pump, the pipe, *I*, is joined to the base of the condenser. As rapidly as the vapors condense they pass into vessel *J* and subsequently, by closing cock *L* and opening *M*, are expelled into *K* from which the liquid is eventually driven into the waste. By noting the quantity of this liquid, the concentration of the sirup in *F* is known at all times.

The question of size of crystals is of the first importance. In general the smaller the crystals the less the "included solvent" or entrapped mother liquor. When the solution in the boiling flask, *F*, has reached the desired concentration, the vacuum is broken at *N* and the solution poured out to crystallize. Crystallization in general does not begin in these pure solutions until they are seeded with a few fine crystals of sugar. This is not done until after the solution is removed from the boiling flask. Two methods of crystallization have been tried. In the first the concentrated solution is transferred to a precipitation jar. It is then carefully stirred with a glass rod provided with a glass shield. This procedure gives satisfactory results so far as the control of the crystal growth is concerned, but it is laborious. In the second, the liquid is transferred to a crystallizer, a cross section of which is shown in figure 99. By this means it was found practicable

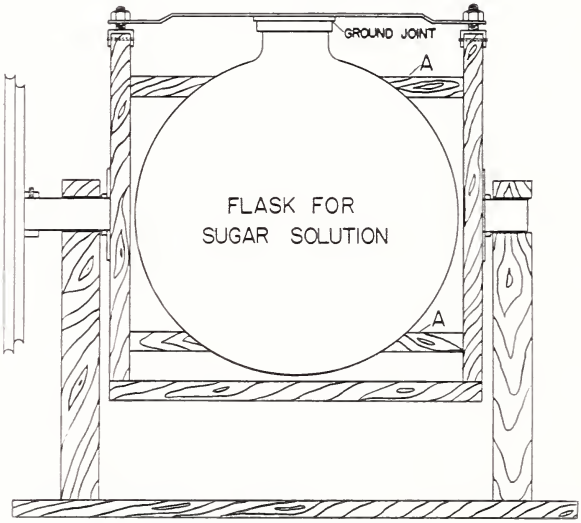

FIGURE 99.—*Crystallizer.*

to crystallize from a larger quantity of liquid and with no danger of contamination. The device is very simple and consists of a hardwood box mounted on bearings and driven by an electric motor. The supports, *A*, *A*, which carry the container, are adjustable in order to keep the center of gravity on the axis of rotation. The box is rotated slowly so that the contents are subjected to a gentle and continuous agitation.

The solid is separated from the mother liquor by a motor-driven centrifugal machine. The centrifuge shown in cross section in figure 100 was built in cooperation with the Bureau, and has met all requirements. Its height over-all is 2 ft, and it requires but 4 square feet of floor space. All the inside walls of the metal housing, in fact all surfaces with which either the crystals or the mother liquor can come in contact, are silver- or nickel-plated. The basket is carried on the end of the vertical shaft of a three-fourths horsepower motor. It has an inside diameter of 9½ inches, and is capable of carrying 10 pounds of sugar. Its heavy cover is held in place by a number of set screws, *A*, *A*, and

is readily removable in order to facilitate the removal of the centrifuged material. The problem of a suitable lining has given considerable trouble. To be satisfactory it must retain very small crystals, permit free drainage of the mother liquor, and be able to stand the severe strains incidental to high speeds. It is obvious that no single lining is available that will meet all three requirements. A built-up lining was accordingly resorted to. It consists of two layers. The outer one is the regular copper centrifuge lining with elongated conical holes. The inner one is of 200-mesh brass gauze. Both linings are silver-plated.

In order to hold the flimsy gauze in place, it was necessary to fold it over the edge of the heavy copper lining, both above and below, and

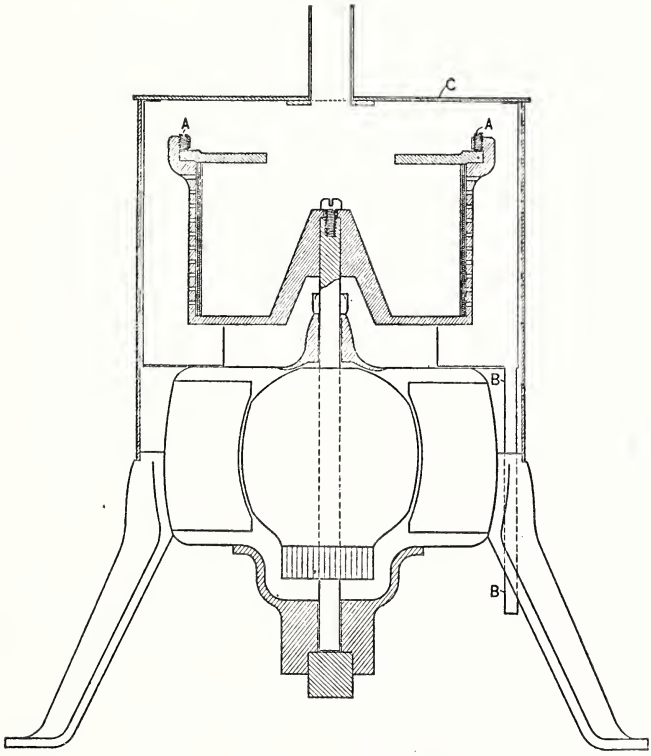

FIGURE 100.—*Centrifuge.*

also around the ends where the vertical edges meet, in every case allowing it to overlap by 1 or 2 cm. At the junction of the two edges an extra piece of gauze was fastened to close the crack. Inasmuch as the wear on the gauze lining occurs at the top, it was protected by a piece of thin copper tape which was bent into place. This combination has given excellent results. The mother liquor finds an outlet through the drain, *B*. The small space left between the lid and the frame was closed by stretching a rubber band tightly around the whole machine.

It will be observed that when the centrifuge is in operation with the hinged lid, *C*, closed, the contents of the basket, as well as the

mother liquor, are safe from contamination by the air of the room. The speed of rotation of the basket is controlled by a rheostat in series with the motor.

In order to secure a proper distribution of the crystals and insure smooth running of the basket, the crystal mass is introduced while the machine is stationary or running at very low velocity. The speed is gradually increased as the mother liquor runs off, until finally the maximum speed of 3,000 revolutions per minute is attained.

The substance is then recrystallized in a similar manner, but a second filtration is accomplished through the layer of asbestos in a glass filter, shown in figure 98, connected directly to the boiling apparatus which supplies the necessary vacuum. This asbestos filter effectively removes the shreds of filter paper which are almost invariably in the filtrate after a filtration through paper. After the solution has passed this filter, it comes in contact with nothing but clean glass, and all manipulation of the solution or crystals is carried out under glass cabinets, to reduce possible contamination with dust. The air-dried crystals are powdered to dust in an agate mortar, of which the pestle carries a shield to prevent contamination, and are placed in a vacuum desiccator over lime.

(e) MODIFICATION OF METHOD OF BATES AND JACKSON [5]

A modification of the method of Bates and Jackson has been tried at this Bureau. A 50 percent solution is clarified with alumina cream, filtered and boiled below 35° C as described above. The boiling is continued to a concentration of 70 to 73 percent of sugar. It is then poured into a crystallizing jar and precipitated by the addition of an equal volume of pure alcohol. The precipitate is separated centrifugally, washed with alcohol, and air-dried. This process is repeated. Before bottling, it is dried over lime in a vacuum.

The alcohol used for the precipitation of pure sugar should be highly purified with respect to acids or aldehydes. It is not essential that it be dry or free from other members of the alcohol group. The method of purification described by Dunlap [6] meets these requirements. Dissolve 1.5 g of silver nitrate in 3 ml of water, add to a liter of 95 percent alcohol in a glass-stoppered cylinder and shake. Dissolve 3 g of caustic potash in 10 ml of warm alcohol, and after cooling pour slowly into the alcoholic $AgNO_3$ solution. Do not shake. Allow to stand overnight. Siphon off and distill.

(f) ANALYSIS

If sugar is to be used for the purpose of standardizing instruments, its purity should be ascertained. This is particularly true of samples required for polarimetric standards and for scientific data of all kinds. There are many sorts of impurities whose presence, if undetected, may lead to false conclusions in the interpretation of data. These impurities may be grouped into classes for the sake of convenience: (a) Soluble inorganic impurities, (b) soluble organic impurities which reduce alkaline copper, (c) soluble organic impurities which do not reduce alkaline copper, and (d) moisture.

Inorganic impurities may readily be recognized by an ash determination. To perform this, a quantity of the sugar should be weighed into a very carefully weighed platinum capsule and burned to a char.

The char should then be ignited in a muffle furnace at a low red heat, properly below 550° C, until the carbon has been consumed. The ash from a sample of properly purified sugar should not amount to 0.01 percent. It must be ascertained that the dish itself is of constant weight during a similar period of heating. Samples prepared at this Bureau have an ash content of less than 0.1 mg for a 5-g sample.

The estimation of very small quantities of reducing substances in the presence of the very large quantity of sucrose requires the employment of special methods. The usual methods in which copper sulfate is dissolved in caustic alkali are unsuitable because of the destructive action of the reagent upon the sucrose.

Bates and Jackson [5] have made a detailed study of the reducing action of pure sucrose on other alkaline copper reagents in which the concentration of the hydroxyl ion was diminished. They found that after several recrystallizations of the sucrose a minimum value for the reduced cuprous oxide was obtained with each of the reagents investigated, and that further recrystallizations failed to lower this value. It appeared, therefore, that either a constant quantity of reducing sugar was present, distributing itself in a constant ratio between crystals and mother liquor, or sucrose itself effected the slight reduction of the copper. From this indirect method they concluded that if any reducing substance other than sucrose itself was present in their purified samples it was of the order of 0.001 percent and entirely negligible for most purposes. Of the several methods studied, Bates and Jackson found a modification of the Soldaini method to yield the most satisfactory results. The modified method is as follows:

Dissolve 297 g of $KHCO_3$ and 1 g of $CuSO_4.5H_2O$ in water and dilute to 1 liter. The potassium bicarbonate should not contain much K_2CO_3. Transfer 50 ml of this solution to a beaker, boil for 1 minute, add a solution containing 10 g of the sugar, bring the whole to boiling, and continue the boiling for exactly 2 minutes. At the end of this period add 100 ml of cold, recently boiled distilled water and collect the precipitate on a Gooch-Monroe crucible or on a very closely packed asbestos mat. Under this procedure it has been shown that 10 g of pure sucrose produces 1.1 mg of Cu_2O, while each 0.01-percent impurity of reducing substance, estimated as invert sugar, increases this precipitate by 1.9 mg.

Another method applicable to the estimation of very small quantities of reducing sugars in pure sucrose is that of Ofner, see page 193.

The soluble organic impurities, which do not reduce alkaline copper, are not so easily detected, but investigations at this Bureau have shown that recrystallization from aqueous solution or by precipitation with alcohol results, in every case examined, in a purification of the sucrose. This fact can only be shown by a polarimetric study.

In order to dry pure, powdered sucrose, care should be exercised not to subject the sample to a prolonged high temperature. Under the influence of an elevated temperature, sucrose undergoes a decomposition which is similar to a process of "caramelization." In table 44 is given the time at each temperature required to form "caramel" equivalent in reducing power to 0.01 percent of invert sugar. Caramel can be detected by its reducing action on the alkaline copper solution. Finely pulverized sugar can be dried at 70° C in a vacuum in 4 hours.

323414°—42——27

The moisture remaining will in general amount to less than 0.003 percent.

TABLE 44.—*Time required at various temperatures to form caramel equivalent to 0.01 percent of invert sugar*

Temperature	Time
°C	*Hours*
79.5	0.57
66.6	10.9
50.0	107.0
39.0	476.0

3. LEVULOSE

(a) PREPARATION OF INULIN

Inulin can be prepared most satisfactorily from dahlia tubers, or in somewhat lower yield from chicory, or in much lower yield from jerusalem artichokes. The most suitable time for the extraction is early autumn, but in the case of dahlias the large clumps of tubers are usually divided for replanting in the late spring and the "blind" tubers which are unsuitable for planting are then available for inulin extraction. Even as late as early summer inulin can be obtained from healthy tubers.

Comminute the tubers or roots in a food chopper or similar appliance and express the juice with a tincture press, using, if necessary, a small proportion of water to complete the extraction. Heat the juice to 60° or 70° C and add milk of lime to about pH 8. Filter and adjust the pH to 7.0 with oxalic acid. Heat to 70° to 80° C, add active carbon, and filter. Allow the filtrate to stand quiescent overnight, during which time the inulin separates in the form of small spheroids. Slightly increased yields can be obtained by placing the filtrate in a refrigerator and still greater yields by completely freezing it and allowing it to thaw at low temperature. Filter the separated inulin with suction and wash with abundant quantities of cold water.

The moist cake of inulin has at this point a dry-substance content of 35 to 40 percent. It can be purified by dissolving in hot water to a concentration of about 15 to 18 percent, treating with carbon, refiltering, and allowing to separate again by chilling. Filter and wash with cold water.

For many purposes it is a satisfactory procedure to spread the moist inulin cake on a glass plate and allow it to dry in air. When dried in this way, it takes the form of hard hornlike masses which can be pulverized readily in a mortar or ball mill. The air-dried substance contains about 10 percent of water of hydration and a small quantity of inorganic impurities. The latter can be diminished to negligible proportions by repeating the processes of solution and chilling, or by electrodialysis.

To avoid the formation of hornlike masses, the moist inulin cake can be washed with 95 percent alcohol, followed by absolute alcohol. The substance, however, has a tendency to retain alcohol [7], which conceivably displaces in part the water of hydration.

A procedure described by Tollens and Elsner [8] is probably suitable for less pure materials than fresh dahlia juices. The juice is expressed

in the presence of calcium carbonate, fermented at 25° C. with bakers' yeast, defecated with lead acetate, and filtered. After removal of the excess lead with hydrogen sulfide, the filtrate is frozen and thawed to cause the separation of inulin.

Inulin crystallizes in the form of doubly refracting sphero-crystals whose crystalline structure is indicated by X-ray patterns [9]. In aqueous solution inulin has a specific rotation, $[\alpha]_D = -39$ to -40 referred to anhydrous substance.

If heated in glycerine, or glycol, or even in water solution and precipitated from these solutions by alcohol, inulin occurs in a form soluble in cold water [7, 10]. This soluble form is also produced by the action of carbon dioxide [11].

(b) PREPARATION OF LEVULOSE

Levulose can be prepared from inulin, or invert sugar, or directly from the expressed juices of inulin-bearing plants. The sugar can, with some difficulty, be crystallized directly from hydrolyzed inulin, but from the two latter sources it must, after hydrolysis, be isolated by means of the insoluble calcium levulate, $CaO.C_6H_{12}O_6.xH_2O$.

(1) Hydrolyzed Inulin.[35]—To 100 g of hydrated inulin add 400 g of water and agitate, preferably with a motor-driven stirrer, until the inulin is "swollen" to a uniform paste. Heat to nearly boiling and allow the inulin to dissolve completely, adding more water if necessary. Reduce the temperature to 60° C and make the solution 0.08 *N* with sulfuric acid. Maintain the solution at 60° for 2½ hours, preferably following the hydrolysis by polariscopic observation of samples withdrawn from time to time. Neutralize by agitating vigorously with barium carbonate in excess or by cooling and titrating to exact neutrality with barium hydroxide, preferably leaving the solution very slightly acid (that is, acid to bromthymol blue). Filter with carbon and evaporate in a vacuum to a thick sirup. Add absolute alcohol and evaporate again to a sirup to remove the remaining water. Extract the sirup with several portions of hot absolute alcohol. Allow the combined extracts to stand for 12 to 24 hours and decant the solution from the sirupy residue which forms. Inoculate with levulose crystals and allow the crystallization to become complete (usually within 2 or 3 days). The yield of sugar is usually relatively small.

(2) Preparation of Invert Sugar.—Dissolve 250 g of pure cane sugar in 846 ml of water and heat to 70° C in a water bath. Add 20 ml of 5 *N* hydrochloric acid, mix, and allow the solution to remain at this temperature for 35 minutes. Cool and neutralize the solution with dilute sodium hydroxide, avoiding local alkalinity. The solution whose volume can be measured now contains 263.16 g of invert sugar, one-half of which is levulose.

(3) Hydrolysis of Plant Juices.—Juices extracted from inulin-bearing plant tubers or roots contain from 12 to 20 percent of dry substance depending upon the composition of the original juice and upon the quantity of maceration or diffusion water used for extraction. The polysaccharides contained in the juice are hydrolyzed,

[35] This method is essentially that of M. Hönig, S. T. Schubert, and L. Jesser [Monatsh. **8**, 529 (1887) **9**, 562 (1888); Ber. deut. chem. Ges. **20**, 721R and **21**, 663R]; and Wohl, [Ber. deut. chem. Ges. **23**, 2084 (1890)] but modified by the substitution of more definite directions for the hydrolysis of inulin [Jackson and Goergen, BS J. Research **3**, 29 (1929) RP79].

preferably with sulfuric acid. It has been found impracticable to supply exactly defined conditions for this hydrolysis, since varying types of juice require variations of conditions. These variations arise from the fact that the acid is in great part rendered inactive by the buffering action of certain impurities in the juice. Even when the pH of different types of juice is made apparently the same, differences in the rate of hydrolysis occur. It is, therefore, necessary to follow the hydrolysis by means of polariscopic or reducing-sugar analysis of samples withdrawn from time to time. Typical hydrolysis data are given in table 45, in which N is the normality of sulfuric acid calculated from the amount of acid actually added; C_{H^+}, the normality of hydrogen ion calculated from the pH measurement (quinhydrone electrode); k, the velocity constant in terms of common logarithms and minutes; and "time 99 percent," the time required for 99-percent hydrolysis.

TABLE 45.—*Hydrolysis of plant juices*

Brix	N	pH	C_{H^+}	Temperature	k	Time, 99 percent
				° C		*Minutes*
12.4	0.20	1.578	0.0264	73.5	0.0231	87
13.7	.25	1.670	.0214	72.0	.0143	140
13.7	.18	2.243	.0057	72.0	.00471	425

The last two measurements were made on the same juice, and it is evident that the velocity is not proportional to the apparent hydrogen-ion concentration, the explanation probably being that the pH measurement is subject to errors caused by impurities in the juice. No difficulty is encountered, however, if the hydrolysis is followed analytically. The time required for 99-percent hydrolysis can be diminished at will by raising the temperature of reaction.

When the hydrolysis is complete, the solution is cooled to room temperature or below and treated with milk of lime to pH 7 to 8 with vigorous agitation and finally filtered.

The filtered juice is analyzed for total reducing sugar and levulose. In precise work the Lane and Eynon titration and a method selective for levulose are used (see p. 205). In approximate work, which is satisfactory in most cases, the Lane and Eynon titration method and the direct polarization are used (see the Mathews formula, p. 223).

(4) PRECIPITATION OF CALCIUM LEVULATE [12].—Prepare a milk-of-lime suspension, magnesia-free, of 18 to 20 percent calcium oxide content and calculate the volume or weight required to contain an amount of calcium oxide equal to 45 or 50 percent of the levulose in the juice. Dilute either the juice or milk of lime so that when the equivalent quantities are mixed, the levulose shall be approximately 6 percent of the total mixture.

The details of procedure for precipitating the calcium levulate have been directed to the end of obtaining relatively large discrete crystals rather than the fine interlacing needles produced in the original method of Dubrunfaut. The precipitation preferably is made in a vessel equipped with a motor-driven stirrer and immersed in a cold bath. The following procedure illustrates the principal features of the

method and is subject to obvious variations with respect to details.

Transfer to the precipitation vessel about one-tenth of the total quantity of milk-of-lime suspension and add one-tenth of the total volume of sugar sirup, allowing the latter to run in at a slow regular rate. It is advisable to examine the precipitate under the microscope from time to time and ascertain that the calcium levulate has formed discrete crystals. When properly prepared, they take the form of elongated prisms. Add successively the remaining portions of milk of lime, each being followed by the respective portion of sirup. Under favorable conditions the levulate crystals will be 0.1 to 0.2 mm in length and can be readily and rapidly separated from the waste water by filtration methods.

The yield of levulose by this process is dependent upon many circumstances. In order to obtain high yields, the temperature of precipitation must be in the neighborhood of 0° C. Increased temperature causes a considerable diminution in the yield of levulose. Thus, in a series of experiments on hydrolyzed artichoke juices, Jackson and Mathews [13] obtained a recovery of 82.3 percent at 3.2° C. 76.2 at 10.7° C, and but 64.0 at 16.0° C.

Typical quantitative data on the precipitation of calcium levulate from various juices are shown in table 46.

It will be observed that the "Total recovered" of each product (lines 16, 22, and 28) approximates the amount taken in the reaction mixture (lines 12, 18, and 24). The yield of levulose (line 33) varies inversely as the solubility of calcium levulate in the juice. The solubility of calcium levulate is greatly increased in the presence of nonlevulose sugars. Thus, in experiment 1, the levulate in the waste water, expressed as levulose (line 13), is held in solution largely by the dextrose. In the remaining experiments, it is dissolved both by dextrose and by other nonlevulose sugars.

TABLE 46.—*Quantitative data on*

Line	Item						
1	Experiment	1		2		3	
2	Type of juice	Pure sugars		Artichokes		Artichokes	
3	Temperature of reaction (° C)	0.0		1.0		1.5	
4	Weight of products, grams:						
5	Reaction mixture	1,811		1,554		1,715	
6	Waste water	1,199		934		1,121	
7	Wash	724		731		676	
8	Levulate cake	426		444		349	
9	Wash water	(538)		(555)		433	
10	Product balances:						
11	Levulose:	%	g	%	g	%	g
12	Reaction mixture	5.38	97.4	8.12	126.1	6.20	106.3
13	Waste water	0.23	2.8	1.04	9.7	0.91	10.2
14	Wash	.23	1.7	0.71	5.2	.65	4.4
15	Levulate cake	21.84	93.0	24.10	107.0	26.58	92.8
16	Total recovered	------	97.5	--------	121.9	--------	107.4
17	Total reducing sugar:						
18	Reaction mixture	6.55	118.6	10.42	161.9	6.82	117.0
19	Waste water	1.56	18.7	3.70	34.6	2.02	22.7
20	Wash	1.10	7.9	2.19	16.0	1.32	8.9
21	Levulate cake	21.84	93.0	24.10	107.0	26.58	92.8
22	Total recovered	--------	119.6	--------	157.6	--------	124.4
23	Total CaO:						
24	Reaction mixture	2.53	45.7	3.45	53.6	3.66	62.9
25	Waste water	0.37	4.4	1.01	9.4	0.69	7.7
26	Wash	.30	2.2	0.62	4.5	.47	3.2
27	Levulate cake	9.08	38.7	8.70	38.6	14.75	51.5
28	Total recovered	--------	45.3	--------	52.5	--------	62.4
29	Ratio, levulose to total reducing sugar:						
30	Reaction mixture	0.822		0.779		0.910	
31	Waste water	.150		.281		.448	
32	Wash	.209		.325		.494	
33	Yield of levulose, percent	95.5		84.8		87.3	
34	CaO required (theoretical), grams	35.5		47.2		43.4	
35	CaO used, grams	45.7		53.6		62.9	
36	Ratio, CaO to reducing sugar in waste water	0.235		0.272		0.339	

calcium levulate precipitation

												Line
4 Artichokes 3.0		5 Artichokes 0.5		6 Chicory 3.0		7 Dahlias 0.8		8 Artichokes 10		9 Artichokes 9.5		1
												2
												3
												4
1,735		1,448		1,644		1,549		1,566		1,838		5
1,170		849		993		770		1,050		1,234		6
705		795		702		675		589		605		7
382		406		462		592		394		387		8
(522)		600		(513)		488		472		400		9
												10
%	g	%	g	%	g	%	g	%	g	%	g	11
5.88	102.0	5.60	81.2	7.04	115.7	8.92	138.2	6.01	94.2	5.94	109.1	12
0.73	8.5	0.58	4.9	0.84	8.4	0.56	4.3	1.25	13.1	1.17	14.4	13
.47	3.3	.45	3.6	.69	4.8	.49	3.3	0.86	5.1	0.85	5.1	14
23.5	89.6	17.71	72.0	21.90	101.2	22.02	130.4	19.29	76.0	22.80	88.2	15
-------	101.4	-------	80.5	-------	114.4	-------	138.0	--------	94.2	--------	107.7	16
												17
6.80	118.0	6.40	92.8	8.02	131.8	9.55	147.9	8.29	129.9	6.92	127.1	18
1.67	19.5	1.52	12.9	1.88	18.7	1.20	9.3	3.55	37.3	2.23	27.5	19
1.08	7.6	1.00	7.9	1.39	9.8	1.02	6.9	2.34	13.8	1.77	10.7	20
23.5	89.6	17.71	72.0	21.90	101.2	22.02	130.4	19.29	76.0	22.80	88.2	21
-------	116.7	-------	92.8	-------	129.7	-------	146.6	--------	127.1	--------	126.4	22
												23
2.71	47.1	3.71	53.7	3.23	53.0	4.00	62.0	3.37	52.7	3.51	64.6	24
0.73	8.5	0.58	4.9	0.67	6.6	0.62	4.7	1.01	10.6	0.68	8.4	25
.49	3.5	.40	3.2	.51	3.6	.51	3.5	0.71	4.2	.51	3.1	26
9.00	34.4	11.40	46.3	9.00	41.6	9.06	53.6	10.1	39.8	13.00	50.5	27
-------	46.4	-------	54.4	-------	51.8	-------	61.8	--------	54.6	--------	62.0	28
												29
0.864		0.874		0.878		0.935		0.725		0.858		30
.439		.384		.448		.424		.352		.522		31
.439		.450		.493		.487		.369		.48		32
87.8		88.7		87.5		94.3		80.7		80.7		33
39.9		30.5		41.7		48.7		38.4		38.9		34
47.1		53.7		53.0		62.0		52.7		64.6		35
0.438		0.383		0.356		0.511		0.285		0.304		36

Dextrose alone at 0° C holds in solution about one-fifth of its weight of levulose (in the form of levulate). Other nonlevulose sugars are derived from inulin, which upon acid hydrolysis yields, in addition to about 92 percent of levulose, 3 percent of dextrose and about 5 percent of a group of nonreducing difructose anhydrides [14]. It is due mainly to these latter substances that the waste water (line 13) from the plant juices contains so much more levulose than that from the mixture of pure sugars. Other nonlevulose sugars may be derived from too prolonged hydrolysis of the juices, which causes the formation of the levulosans described by Pictet and Chavan [15], or from a too alkaline medium for defecation, which may cause the Lobry de Bruyn-van Ekenstein transformation.

Table 46 shows in general the compositions of products and by-products which would probably be found in a levulose plant of any magnitude.

The levulate cake, which contains in average about 22 percent of levulose and 10 percent of calcium oxide, is carbonated by adding it in small portions to a violently agitated quantity of cold water into which carbon dioxide is passed, preferably by some device such as the Doherty carbonator [16] which disperses the gas into a fine state of division. Carbonation is continued until the solution is slightly acid to phenolphthalein. The mixture at this point necessarily contains a considerable quantity of calcium bicarbonate which requires neutralization, since, if carried into the filtrate from the calcium carbonate, it would be decomposed during the subsequent evaporation by volatilization of carbon dioxide. When calcium bicarbonate is decomposed in this manner, it imparts a pH of 8 to 9 to the levulose solution. This alkalinity at the temperature of evaporation impairs the sugar seriously.

The most satisfactory method of neutralizing calcium bicarbonate is to add a thin suspension of milk of lime or calcium levulate until a minimum electrical conductivity is reached. The calcium carbonate, which at the low temperature sometimes crystallizes with six molecules of water of crystallization, is filtered and washed. The filtrate is now slightly alkaline, being saturated with calcium (and if present, magnesium) carbonate. It is again adjusted to a minimum electrical conductivity by addition of dilute oxalic acid.

The filtrate is evaporated at reduced pressure to a sirup. At some point during the evaporation there usually occurs a separation of inorganic salts, which are removed by filtration with 1 or 2 percent of active carbon. The resulting solution should have a levulose purity in excess of 99 percent, being contaminated mainly by inorganic salts in which magnesia usually predominates.

(5) Crystallization of levulose.—Crystallization of the sugar can be conducted in aqueous or in aqueous alcoholic solution. For laboratory preparations, aqueous alcohol is the more convenient solvent. The solution is evaporated to a sirup and crystallized, after seeding, under the conditions illustrated in table 47. These conditions of course may be considerably varied.

TABLE 47.—*Recrystallization of levulose from alcoholic solution*

n_D^{20} thick sirup	Levulose	Weight of sirup	Calculated weight of levulose	Strength of alcohol (by volume)	Weight of alcohol	Yield of dry crystals	
						Weight	Percent
	Percent	*g*	*g*	*Percent*	*g*	*g*	
1.508	89.2	897	800	95	346	482	60
1.508	89.2	1,078	962	100	353	735	76
1.5133	91.3	359	328	95	144	211	64

Crystallization is accomplished in a crystallizer or in a tumbling machine or any apparatus which keeps the crystallizing mass in slow continuous motion. Frequently the addition of alcohol causes a separation into two liquid layers which, however, coalesce as crystallization progresses. The crystals are separated on a Büchner filter or by centrifugal drainage and thoroughly washed with 95-percent alcohol.

For the preparation of levulose of highest purity the substance can be recrystallized in the same manner. It sometimes occurs that the inorganic impurities persist. These can be removed by determining the ash content and, considering it as calcium carbonate, adding the stoichiometric equivalent of nitric acid. In this case the final washing with alcohol must be very thorough.

Levulose can also be crystallized from aqueous solution in spite of its high solubility in water. The solution is evaporated at diminished pressure to about 90 percent of solids, placed in a crystallizer at 50° to 55° C, seeded with crystals, and allowed to crystallize in slow motion by letting the temperature drop very gradually over a period of 1 to 3 or 4 days, depending upon the purity of the solution and the rate of growth of the crystals.

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XXVI. PURITY

1. CALCULATION

The "coefficient of purity" is the percentage of sucrose in the solids or dry substance of a sugar product and may be expressed by the formula

$$\text{Purity}=\frac{\text{percent sucrose}}{\text{percent solids}}\times 100 \tag{131}$$

It is also known as the "purity quotient" or more generally as the "purity." If accurate methods are used in the determinations, such as the Clerget for sucrose, and drying for solids, the above ratio is known as the "true purity." This value is used in special research and for purposes of checking or comparing products at different stages of manufacture and should always be recorded and referred to as *true* purity.

Of more general use for purposes of process control in individual factories is the "apparent purity," the value of which is found by dividing the direct polarization of the product in solution by the degrees Brix and multiplying the quotient by 100. Although the apparent purity is only an approximation, it is of great value for comparative purposes because of the rapidity with which the determinations may be made. It is important, therefore, that the analyses for each type of product be performed in exactly the same manner.

The procedure for apparent purity is applied directly to raw or thin juices without weighing or measuring. Solids or massecuites must be dissolved and thick liquors diluted. The solution is diluted with water to a convenient density between 12 and 20 Brix, thoroughly mixed, and allowed to stand in the cylinder until all air has escaped. The removal of air bubbles may be hastened by connecting the cylinder to suction by means of a one-hole stopper and suitable tubing. The degrees Brix is then read using standard hydrometers and thermometers, the reading being corrected to 20° C.

To a portion of the solution (150 to 200 ml) roughly measured, a sufficient amount of anhydrous basic lead acetate is added to clarify. About a teaspoonful of dry diatomaceous earth is added and the whole is thoroughly mixed, and filtered on a rapid filter paper. The clear filtrate may be polarized directly in a 200-mm tube or, if it is deeply colored, in a 100-mm tube. In cane products, varying amounts of invert sugar are present and the negative rotation of the levulose constituent is reduced by the presence of basic lead acetate. The positive rotation of the dextrose is not thus affected, so that the net result is a plus error in rotation.

When the amount of invert sugar is high, the effect of the excess lead may be obviated in either of two ways: (1) After addition of the dry lead salt and shaking, dry powdered oxalic acid is added, a little at a time, until the leaded solution is faintly acid to litmus. The whole is then thoroughly mixed and filtered. The clear filtrate is polarized as above. (2) The filtrate from the solution treated with lead alone (100 ml in a 110-ml flask) is treated with dilute acetic acid until the reaction of the solution to litmus paper is slightly acid. Dilution to the 110-ml mark is completed with water, and the solution is mixed and polarized. The polarization is corrected by adding one-tenth of the observed reading.

In beet products little or no invert sugar is normally present. A solution of basic lead acetate (sp gr 1.25, 20°/20°) is commonly used for clarification instead of the dry salt. To 100 ml of the solution (after determining the Brix) contained in a 100–110 ml flask is added the proper amount of lead solution from a burette. The solution is mixed, a drop or two of ether being added to the flask to disperse the foam, if present, and the volume is completed to 110 ml with water. The solution is then filtered and polarized and the reading corrected by the addition of one-tenth of its observed value.

The apparent purity of a sugar solution may be calculated by means of the formula

$$\text{Apparent purity} = \text{Factor} \times \text{direct polarization}. \tag{132}$$

A formula for obtaining the "factor" to be used in the second term of the above equation was originally elaborated by Cassamajor and was based upon the Mohr cubic centimeter at 17.5° C and the normal weight, 26.048 g. An equation based upon the modern units, milliliters at 20° C and the normal weight of 26.00 g as published by Osborne [1], was derived as follows:

Let

D = true sp gr of solution at 20°/20° (table 109).
D' = apparent sp gr of solution at 20°/20° (table 114, p. 632).
B = degrees Brix of solution, then
$D' = D + 0.001\ (D - 1)$.

$$\text{Factor} = \frac{26.00 \times 100 \times 1.1}{99.72 \times BD'} = \frac{28.680}{BD'} \tag{133}$$

This equation includes the correction for one-tenth dilution and by its use a table of factors was calculated for each 0.1 Brix from 0 to 25, which may be applied in eq 132.

The formula of Rice [2] omits the one-tenth dilution factor and is expressed as follows:

$$\text{Factor} = \frac{26.00 \times 100}{99.718 \times \text{sp gr} \times \text{Brix}}. \tag{134}$$

By means of this equation, Rice calculated a table of factors in increments of 0.1 extending from 0 to 25 Brix. This table (table 146, p. 702) may be used for calculating apparent purity from experimental values of the Brix and polarization.

A convenient table of purity values, expanded from Horne's table as calculated by means of Rice's equation 134 is given by Meade [3]. Here the purity may be read directly from the Brix and polarization of the solution. This table is arranged in intervals of 0.2° S from polarization equals 15 to polarization equals 87.0.

It has already been pointed out that in the determination of "true purity" the sucrose is obtained by the Clerget method and the solids by drying, while in the determination of "apparent purity" the direct polarization and Brix are employed. The above methods are the ones in general use.

However, it is occasionally convenient to use the values for solids obtained from the refractive index in conjunction with either the percentage of sucrose or the polarization. Thus, there are six possible combinations. Noel Deerr [4] suggests the use of the terms "true

purity," "gravity purity," and "refractive purity," when the percentage of sucrose is used as the numerator of eq 131, and solids by drying, by Brix spindle, or by refractometer, respectively, as the denominator. If the polarization is used as the numerator, the terms are qualified by the expression "polarization."

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XXVII. PACKING OF SUCROSE [1, 2, 3]

1. INTRODUCTION

The volume occupied by a given weight of sugar is a matter of importance, both in relation to the operation of the centrifugal station and the bagging of the sugar. It is the sum of the volumes of the actual crystals and of the voids between them, and depends on their size and shape as well as on the way in which they are packed together. A study of the physical factors involved in the packing of sugar has been made by Drinnen [1]. His results are also valuable in that they indicate the way to an improved technique, which is desirable for further study of the problem.

2. CRYSTAL DIMENSION

Sugar crystals were classified into various fractions in accordance with their size, using a set of standard Tyler sieves. The dimensions of the sieved fractions were estimated under the microscope by an eyepiece micrometer. Since the smallest dimension largely determines the sieve in which the crystal remains, this dimension should be the reference size for crystal measurements, provided that the crystals do not depart very greatly from the cubical shape. In table 48 are shown the results from the examination of 50 crystals from each sieve fraction.

TABLE 48.—*Crystal size as related to sieve mesh*

Meshes per inch	Sieve openings	Average grain size	Crystal dimensions (measured)	Meshes per inch	Sieve openings	Average grain size	Crystal dimensions (measured)
	mm	*mm*	*mm*		*mm*	*mm*	*mm*
14	1.168	1.41	1.83×1.47	35	.417	.50	0.70×0.58
20	0.833	1.00	1.14×0.98	48	.295	.36	0.40×0.40
29	.589	0.71	1.01×0.83				

3. VOLUME OF CRYSTALS AND VOIDS

Two methods were used for this determination, (a) displacing the volume of air in a known weight of the sugar by means of a liquid in which sugar is insoluble and measuring the volume, and (b) weighing a known volume of sugar and calculating the volume of the crystals from the weight and specific gravity of the sugar. The former appears

to be the more accurate method. Average percentage figures obtained are shown in table 49.

TABLE 49.—*Volume of sucrose crystals and of interstitial voids as related to sieve mesh size*

Sieve meshes per inch	Method (a)		Method (b)		Sieve meshes per inch	Method (a)		Method (b)	
	Crystals	Voids	Crystals	Voids		Crystals	Voids	Crystals	Voids
	Percent	*Percent*	*Percent*	*Percent*		*Percent*	*Percent*	*Percent*	*Percent*
14	56.0	44.0	56.9	43.1	35	64.6	35.4	65.3	34.7
20	60.4	39.6	62.9	37.1	48	63.4	36.6	66.1	33.9
28	63.3	36.7	65.1	34.9	Over 48	62.4	37.6	66.5	33.5

4. WEIGHT OF CRYSTALS

Grain counts were taken for the various fractions on oven-dried sugar, per gram from each fraction, as follows:

TABLE 50.—*Weight of crystals in relation to average grain size (screen fractions)*

Average grain size	Crystal dimensions	Crystals per gram	Weight per crystal	Average grain size	Crystal dimensions	Crystals per gram	Weight per crystal
mm	*mm*		*mg*	*mm*	*mm*		*mg*
1.41	1.83×1.47	303	3.30	.50	0.70×0.58	4,301	.23
1.00	1.14×0.98	1,070	1.07	.36	.49×0.41	15,057	.70
0.71	1.02×0.83	2,379	0.42				

5. AREA OF THE CRYSTALS

This is a very difficult matter to estimate, and the findings of Pellet, summarized by Thieme [3], are given in table 51.

TABLE 51.—*Relation between weight and surface area of crystals for various crystal sizes (screen fractions)*

Weight per crystal	Surface area	Surface: weight	Weight per crystal	Surface area	Surface: weight
mg	*mm*^{2}		*mg*	*mm*^{2}	
3.28	8.168	2.29	.30	1.353	4.51
1.56	5.136	3.49	.101	0.658	6.51
0.64	2.578	4.01	.057	.467	8.15

6. REFERENCES

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PART 3. PREPARATION AND PROPERTIES OF THE SUGARS AND THEIR DERIVATIVES

XXVIII. OPTICAL ACTIVITY, CONFIGURATION, AND STRUCTURE IN THE SUGAR GROUP

1. CONSTITUTION OF THE SUGARS AND THEIR INTERRELATIONSHIPS

At the dawn of history our aboriginal ancestors were familiar with honey and the sweet exudations of various trees and plants, but the chemistry of the sugars did not begin until the introduction of cane sugar into Europe [1]. With the expansion and development of Europe, the need was felt for a sugar-bearing plant which could be grown in a temperate climate. In the course of the search for a source of sugar, attention was directed to many closely related natural products. Thus, in 1792 Lowitz [2] found that starch on hydrolysis gives a sweet substance, now known as *d*-glucose or dextrose. Many other natural products were found which, on hydrolysis, gave closely related products. These substances, with few exceptions, contain carbon, hydrogen, and oxygen, in the proportions corresponding to a hydrate of carbon, and hence they were named "carbohydrates."

The carbohydrates comprise the sugars and the polysaccharides. The polysaccharides are compounds which, by hydrolysis, yield sugars. The sugars are classified as simple sugars or monosaccharides, and compound sugars comprising the disaccharides, trisaccharides, and tetrasaccharides. The simple sugars are classified further as trioses, tetroses, pentoses, methylpentoses, hexoses, heptoses, etc., according to the number of carbon atoms in the sugar molecule. The hexoses, pentoses, and methylpentoses occur in many plant products and play important roles in many biological processes. The two most important simple sugars are dextrose and levulose.

Few organic compounds have been studied as intensively as the hexoses, and in particular, dextrose. This substance was known in ancient times as grape sugar, but was not isolated from starch until 1792. It was found in diabetic urine in 1815 by Chevreul [3], and in cellulose in 1819 by Braconnot [4]. Crystalline dextrose, however, did not find wide use until a successful method for the production of the hard refined crystalline sugar was devised at the National Bureau of Standards [5]. This method in its essential principles was applied commercially, and many millions of pounds of white crystalline dextrose are now produced annually.

During the latter half of the nineteenth century many organic chemists devoted their attention to the study of dextrose. In 1843 Dumas [6] ascertained that dextrose has the empirical formula CH_2O, and in 1870 Baeyer [7] advanced the structural formula

$$\underset{6}{CH_2(OH)}.\underset{5}{CH(OH)}.\underset{4}{CH(OH)}.\underset{3}{CH(OH)}.\underset{2}{CH(OH)}.\underset{1}{CHO}.$$

This formula was supported by subsequent molecular-weight determinations [8] and by the following chemical reactions: (1) The sugar yields, on oxidation with bromine water or nitric acid, a monocarboxylic acid (gluconic) which contains the same number of carbon atoms as the parent sugar [9],

$$CH_2OH(CHOH)_4CHO + Br_2 + H_2O \rightarrow \underset{\text{(gluconic acid)}}{CH_2OH(CHOH)_4COOH} + 2HBr$$

This proves that the aldehyde or potential aldehyde group lies at one end of the carbon chain. (2) On reduction with sodium amalgam, the sugar yields a hexahydric alcohol [10] (sorbitol),

$$CH_2OH(CHOH)_4CHO + H_2 \rightarrow \underset{\text{(sorbitol)}}{CH_2OH(CHOH)_4CH_2OH}.$$

(3) Reduction of the sugar with hydriodic acid gives *normal* hexyl iodide, which proves that the carbon atoms are combined in a straight chain. (4) The sugar combines with hydrogen cyanide to give a nitrile, which, after saponification and reduction with hydriodic acid, yields a *normal* heptanoic acid,

$$CH_2OH(CHOH)_4CHO + HCN \rightarrow CH_2OH(CHOH)_4\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CN \rightarrow \underset{\text{(normal heptanoic acid)}}{CH_3(CH_2)_5COOH}$$

This confirms the straight-chain formula and shows the presence of an aldehyde or potential aldehyde group [11]. (5) The sugar yields pentaacetyl and other derivatives, indicating the presence of five hydroxyl groups. (6) Treatment with phenylhydrazine gives glucose phenylhydrazone,

$$CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH{=}N{-}NHC_6H_5,$$

and prolonged action gives glucosazone,

$$CH_2OH.CH(OH).CH(OH).CH(OH).\underset{\underset{N-NHC_6H_5}{\|}}{C}-\overset{\overset{H}{|}}{C}{=}NNHC_6H_5.$$

The formation of hydrazones is typical of carbonyl compounds, and the formation of osazones is peculiar to alpha hydroxy aldehydes and ketones. Although these properties support the polyhydroxy aldehydic formula, other properties which will be considered later show that the aldehyde modification is only one of the several tautomeric forms which are characteristic of the sugars. Indeed, the crystalline sugars contain lactol ring structures, and even in solution the quantity of the free aldehyde modification is extremely small.

While the chemistry of dextrose was being developed, a number of other sugars were being investigated. Some of these resemble dextrose in that on oxidation they give acids containing the same number of carbon atoms, whereas others give acids containing fewer carbon atoms. The most important of the latter group is *d*-fructose

or levulose, which has the same molecular weight as dextrose but differs fundamentally in that the reducing group lies on the second carbon. One modification of levulose can be represented by the formula:

$$\begin{array}{l} CH_2(OH).CH(OH).CH(OH).CH(OH).\underset{\underset{O}{\|}}{C}-CH_2OH. \\ \quad 6 \qquad\quad 5 \qquad\quad 4 \qquad\quad 3 \qquad\quad 2 \quad 1 \end{array}$$

This structure is supported by the following evidence: (1) The sugar exhibits the reducing properties characteristic of a carbonyl group, but on oxidation with nitric acid the carbon chain is broken to give tartaric and oxalic acids,

$$CH_2OH.CHOH.CHOH.CHOH.\underset{\underset{O}{\|}}{C}.CH_2OH + HNO_3 \rightarrow$$

$$COOH.CHOH.CHOH.COOH + COOH.COOH.$$

This is evidence that the reducing group lies on either carbon 2 or carbon 3. (2) Reduction with sodium amalgam yields two hexahydric alcohols, "sorbitol" and "mannitol,"

$$CH_2OH.\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\underset{\underset{O}{\|}}{C}-CH_2OH + H_2 \rightarrow$$

$$CH_2OH.\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}.CH_2OH$$

(sorbitol)

$$CH_2OH.\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}.CH_2OH.$$

(mannitol)

The formation of these two products shows that the carbonyl is not on the end of the carbon chain, and the formation of sorbitol from both dextrose and levulose shows that the two sugars are alike except for the groups attached to carbons 1 and 2. (3) Reduction of the sugar with hydriodic acid yields normal hexyl iodide, which proves that the carbon chain is not branched. (4) Treatment with hydrogen cyanide and saponification of the nitrile yields a heptanoic acid which, on reduction with hydriodic acid, gives α-methyl hexanoic acid.

$$CH_2OH(CHOH)_3-\underset{\underset{O}{\|}}{C}-CH_2OH + HCN \rightarrow CH_2OH(CHOH)_3-\overset{CN}{\underset{OH}{C}}-CH_2OH \rightarrow$$

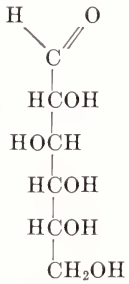
$$CH_2OH(CHOH)_3-\overset{COOH}{\underset{OH}{C}}-CH_2OH \rightarrow CH_3(CH_2)_3-\overset{COOH}{\underset{H}{C}}-CH_3.$$

323414°—42——28

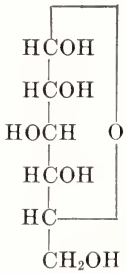
This shows that hydrogen cyanide adds to the second carbon, and therefore the carbonyl is on this carbon [12]. (5) The sugar yields pentaacetates and other products which require the presence of five hydroxyl groups. (6) Treatment with phenylhydrazine gives glucosazone [13], which is further evidence that, except for carbons 1 and 2, dextrose and levulose are alike. In dextrose the reducing group is located on the first carbon, and therefore the sugar is related to the aldehydes, while in levulose the reducing group is located on the second carbon and therefore levulose is related to the ketones. This distinction is the basis for the further classification of the sugars as aldoses and ketoses according to whether the reducing group lies on the end carbon or on an intermediate carbon.

Even though the sugars give many of the reactions of aldehydes and ketones, at least in neutral solutions they do not give certain specific aldehydic and ketonic reactions, such as the red color with Schiff's reagent, or the intense absorption bands in the ultraviolet region, which are characteristic of free carbonyl groups [14]. The absence of these distinctive aldehydic and ketonic properties is supposedly explained by the interaction of the carbonyl group with the neighboring hydroxyl groups to form cyclic hemiacetals.

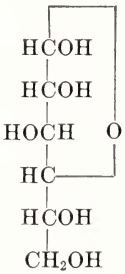
DEXTROSE



Open-chain form.

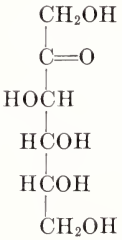


Pyranose form.

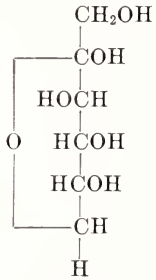


Furanose form.

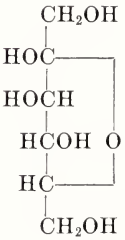
LEVULOSE



Open-chain form.



Pyranose form.

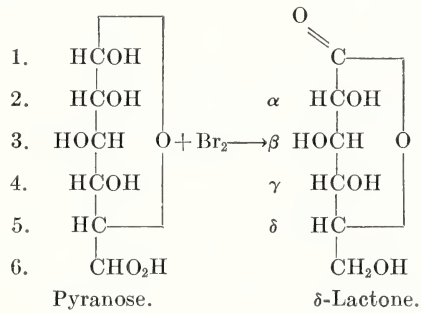


Furanose form.

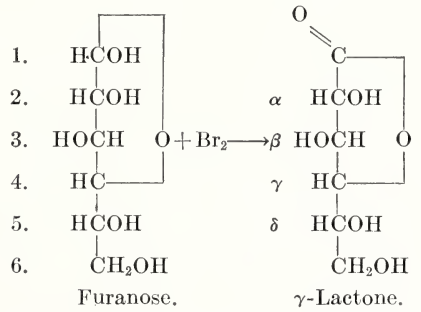
Although the cyclic hemiacetals can be considered as potential aldehydes, they differ fundamentally from the open-chain compounds and exhibit many interesting properties. As early as 1846 Dubrunfaut [15] noted that the optical rotation of freshly dissolved glucose changes

on standing, and he suggested that this change (mutarotation) was due to a change in molecular composition of the sugar [16]. In subsequent years, this explanation received a striking confirmation in the discovery of two forms of this sugar, which, in aqueous solution, spontaneously revert to an equilibrium mixture of the two. Prior to the discovery of the second form of glucose, Colley [17] had suggested that one oxygen atom is combined with two carbon atoms to form a cyclic structure. This idea was taken up by Tollens [18], who recognized that various ring isomers are possible.

Lacking an experimental method for proving the size of the ring, the early workers postulated a 1,4, or furanose ring, for the normal sugars and glycosides, but subsequent work has proved that the normal methyl glycosides and crystalline sugars contain the 1,5, or pyranose ring [19]. Several direct methods are available for determining the structures of the methyl glycosides, but the structures of the free sugars rest on less satisfactory proof. Perhaps the best method for ascertaining the structures of the aldoses is the bromine oxidation method of Isbell and Hudson [20, 21], in which the pyranose and furanose modifications are oxidized to give the delta or gamma lactones, respectively, without rupturing the lactol ring. Presumably the reaction takes place in the following manner:



Pyranose. δ-Lactone.



Furanose. γ-Lactone.

The validity of the method rests on the correct identification of the delta and gamma lactones and on the hypothesis that the ring structure does not change either before or during the reaction. The results obtained by this method and by other methods, such as the comparison of the optical rotations of the sugars with the optical rotations of glycosides of known structure, indicate that the crystalline sugars so far investigated, with the exception of mannose-$CaCl_2 \cdot 4H_2O$

and a few other sugar derivatives, contain the amylene oxide or pyranose ring, while mannose-$CaCl_2.4H_2O$ [22] and lactulose [23] contain the butylene oxide or furanose ring. Sugars which contain the amylene oxide ring are called pyranoses, and those which contain the butylene oxide ring are called furanoses. The reducing carbon in the cyclic sugar is asymmetric, and, therefore, each cyclic sugar exists in two modifications. These modifications are designated alpha and beta (see page 424). The alpha and beta modifications of the various ring forms and the open-chain modification are mutually interconvertible and exist in solution in dynamic equilibrium. The optical rotations of these substances are not alike and consequently, when a sugar is dissolved in water, the optical rotation

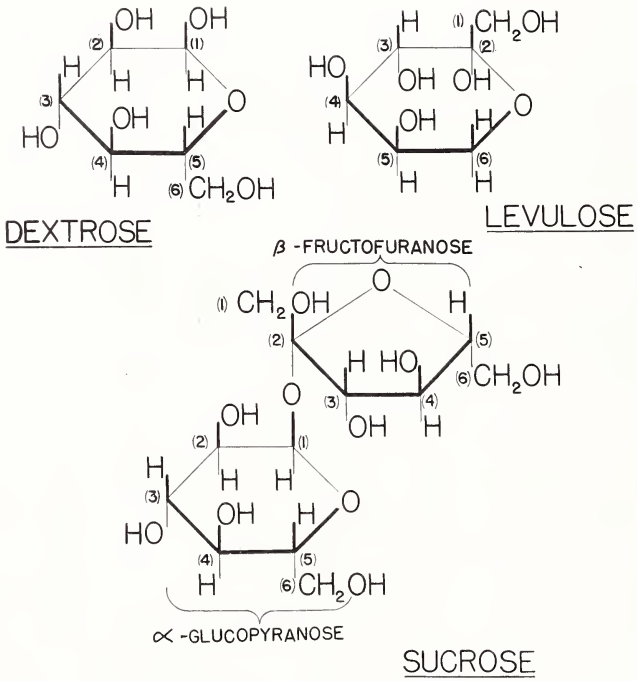


FIGURE 101—*Formulas for dextrose, levulose, and sucrose.*

changes as equilibrium is established between the various modifications. This change in optical rotation is called *mutarotation*, and the reactions involved in establishing the equilibrium state are called the mutarotation reactions. Crystalline dextrose is a glucopyranose, levulose is a fructopyranose, and sucrose is a compound sugar having a fructofuranose in combination with a glucopyranose.

The disaccharide union in sucrose is formed between the carbonyl groups of dextrose and levulose, so that the carbonyl groups are completely blocked; for this reason, sucrose does not give the reactions characteristic of a carbonyl or a potential carbonyl group. From an analytical standpoint, the most important reaction of the carbonyl group is the property of reducing alkaline copper reagents, such as Fehling's solution. A sugar which has this characteristic is called a

reducing sugar. Sucrose, trehalose, melezitose, raffinose, and other sugars in which the carbonyl groups are blocked, do not give the characteristic reducing reactions and consequently they are called *nonreducing sugars* in contrast to the *reducing sugars.* All monosaccharides are reducing sugars. The reducing sugars also include compound sugars which contain a free carbonyl group, as for example, lactose, in which the carbonyl of a galactose radical is combined with the hydroxyl of the fourth carbon of a glucose molecule. This leaves the carbonyl of the glucose constituent free, and consequently the sugar has the reducing properties characteristic of the carbonyl group. Likewise, maltose, cellobiose, and gentiobiose are merely substituted glucoses and contain free carbonyl groups. The disaccharide union in these compounds is analogous to that found in certain products known as glycosides. The term "glycosides" is generic, while the terms "glucosides,"[36] "galactosides," "mannosides," etc., refer to glycosides of specific sugars. The glycosides are relatively stable compounds and for this reason they are particularly useful in the study of the structures of the sugars. The formulas of the individual sugars and their stereoisomeric relations will be considered in more detail after the subject of optical rotation in relation to molecular structure has been discussed.

2. OPTICAL ACTIVITY IN ORGANIC COMPOUNDS

Optical rotation measurements are particularly useful for providing information concerning the arrangement of the atoms in space and the character of the atomic linkage. Some substances are optically active in the crystalline state only, while others are optically active in the crystalline, gaseous, liquid, or dissolved state. The optical activity of the first group is due to the structure of the crystal, while the optical activity of the second group is due to dissymmetry of the molecule. From the time of Van't Hoff and Le Bel to the present, advances in stereochemistry have shown that the only substances which exhibit optical rotation in solution are those whose molecules are dissymmetrical. Molecular structure depends primarily on the arrangement in space of the groups which are covalently linked to an atom. The chemical and physical properties of the elements show that the valences of a group of four are directed toward the corners of a tetrahedron, a group of six toward the corners of an octahedron, and a group of eight toward the corners of a cube [24]. Although optically active substances are known to be derived from many elements, those of carbon are the most important. Nearly all of the optically active organic compounds contain one or more asymmetric carbon atoms. An *asymmetric carbon* has four valences, which are satisfied by combining with four different atoms or groups of atoms. As may be seen from diagrams I and II in figure 102, a tetrahedral atom combined with four different groups, *a*, *b*, *c*, *d*, can occur in two, and only two, distinct stereoisomeric modifications.

Substances containing asymmetric carbons are characterized by the fact that they are not identical with their mirror images. This may be observed from diagrams I and II of figure 102. Two substances whose molecules are related as object and mirror image are called

[36] The early workers used the term "glucoside" in the generic sense, but this use has been largely abandoned.

optical antipodes, or enantiomorphs, and have like physical and chemical properties, except for those properties which are characterized by directional components. Thus the optical rotations of enantiomorphs are of like degree but of opposite direction; frequently, but not always, their crystals are mirror images. Their reactions with symmetrical molecules are alike, but their reactions with dissymmetrical molecules take place at different rates, and if the dissymmetry is not destroyed, they give different products. If equal quantities of enantiomorphs are mixed, the optical rotation of one neutralizes the optical rotation of the other, with the result that the product appears to be optically inactive. Products containing equal quantities of enantiomorphic substances are described as racemic. When the enantiomorphs form a definite compound the product is known as a racemic compound. The crystal structures, melting points, solubilities, and energy contents of racemic compounds are different from those of the constituents. In many respects racemic compounds resemble double salts; in solution they dissociate, give

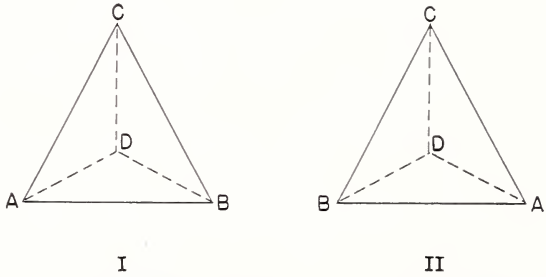
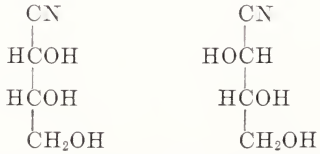


FIGURE 102.—*Stereoisomeric modifications of an asymmetric carbon atom.*
A, *B*, *C*, and *D* indicate the corners of the tetrahedron.

abnormal molecular weights, and exhibit the properties of the constituent isomers. Some enantiomorphs do not yield true racemic compounds, but give merely mixtures. In the absence of dissymmetric substances, synthetic reactions leading to the production of asymmetric carbons give racemic products because of the equal probability of the formation of either isomer. However, should one of the reacting substances be optically active, the introduction of another asymmetric center results in products which are not related as object and mirror image. For example, if *d*-glyceraldehyde is treated with hydrogen cyanide, nitriles of erythronic and threonic acids are produced in unequal quantities because *d*-glyceric aldehyde is dissymmetric, and hence the probability of the formation of one isomer is greater than the probability of the formation of the other. The two nitriles are not identical and are not mirror images; they have char-



d-Erythronic nitrile. *d*-Threonic nitrile.

acteristic properties and are separate and distinct compounds. Compounds of this character are called *diastereoisomers*. The number of diastereoisomers which can be obtained for any structure depends on the number of asymmetric carbons present in the molecule and on whether the two ends of the molecule are alike. If the ends of the molecule are different, two asymmetric carbons give rise to four isomers and three asymmetric carbons give rise to eight isomers, but if the ends of the molecule are alike, the number is less. For example, tartaric acid contains two asymmetric carbons and exists in the three modifications represented by the formulas:

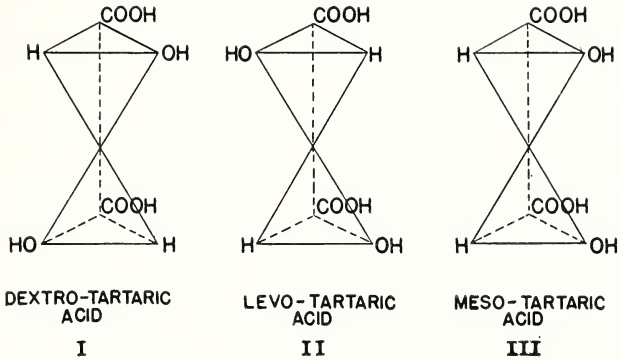


FIGURE 103.—*Modifications of tartaric acid.*

The two modifications represented by formulas I and II are enantiomorphs. A mixture of these modifications crystallizes in a racemic compound known as "racemic acid." Racemic compounds are optically inactive by *external* compensation. The modification of tartaric acid illustrated by formula III is fundamentally different from the modifications illustrated by formulas I and II. Examination of the structural model of formula III reveals that the upper asymmetric carbon is the mirror image of the lower. On account of this relationship, the upper asymmetric carbon rotates the plane of polarized light by a certain amount to the right or left, while the lower asymmetric carbon rotates the plane of polarization by an equal amount in the opposite direction, with the result that the net rotation is zero. Substances which are optically inactive through *internal* compensation in this manner are designated by the prefix *meso*, whereas *racemic* mixtures and compounds which are optically inactive by *external* compensation are designated by the prefix *dl*.

The enantiomorphic modifications of an optically active substance are distinguished by the single prefix *d* or *l*. The prefixes *d* and *l* were originally used, and in many fields are still used, to indicate whether the substance rotates the plane of polarization in the dextro (clockwise) or in the levo (counterclockwise) direction. Classification according to the direction of the optical rotation frequently leads to contradictory names for closely related substances. For example, gluconic acid prepared from dextrose is levorotatory, its lactones and alkali and alkaline earth salts are dextrorotatory, and its lead and nickel salts are levorotatory. Furthermore, substances are known which are dextrorotatory in one solvent, or at one temperature, and levorotatory in a different solvent or at a different temperature.

To avoid confusion, in the carbohydrate field enantiomorphic modifications are classified according to *configuration* rather than according to optical rotation. For example, dextrose and levulose are designated *d*-glucose and *d*-fructose, respectively, notwithstanding the dextrorotation of one and the levorotation of the other. Enantiomorphs are classified by comparison with reference compounds. Emil Fischer used *d*-glucose as his reference compound, but this led to ambiguity because the reference compound contains several asymmetric carbons. The classification in present use, originated by Rosanoff, [25] avoids this complication by making dextrorotatory glyceraldehyde the reference substance. According to this system, the sugars which have the same configuration for the terminal asymmetric carbon as that of dextrorotatory glyceraldehyde are classified in the *d* series, whereas those which have the reverse configuration are classified in the *l* series. The terminal asymmetric carbon is defined as the asymmetric carbon farthest from the reducing group, or the one adjacent to the CH_2OH group if this group is present. This classification is not satisfactory for those sugar derivatives in which both ends of the molecule are alike. For example, the same dibasic acid is obtained from *d*-glucose and from *l*-gulose. In such cases the classification is taken from the more important sugar. Thus the dibasic acid derived from *d*-glucose is called *d*-saccharic acid.

It is necessary to distinguish between the use of *d* and *l* in the carbohydrate field and the use of *d* and *l* in other fields of stereochemistry. Levorotatory tartaric acid has the *d*-glyceraldehyde configuration; hence, according to Rosanoff, it becomes *d*-tartaric acid in contrast to its old and established name, *l*-tartaric acid. Confusion can be avoided by using the symbol *d* (—), in which *d* signifies the configuration and (—) the optical rotation. Most amino acids obtained from proteins have the same configuration as *l*-glyceric acid and belong in the *l*-series; but many exhibit dextro optical rotations and are frequently called *d* acids. Some authors use capital *D* or *L* to signify configuration and reserve the small letters for indicating optical rotation. Unfortunately the small letters have been used indiscriminately for rotation and configuration and at present no uniform practice is established. Since the configurations for the hydroxy acids, the amino acids, and the sugars and their derivatives have been established, the time is ripe for the adoption of a uniform system.[37]

3. STEREOISOMERISM OF THE SUGARS

Our knowledge of the configuration of the carbohydrates has been developed with the use of three dimensional models, based on the concepts of Van't Hoff and Le Bel, and therefore the results of investigations in this field must be construed in relation to these models. The models are represented in print by the projectional formulas originated by Emil Fischer [26]. To obtain a projectional formula, the molecular model is held in front of a sheet of paper, with the reducing group at the top of the sheet and with the asymmetric carbon under consideration placed so that its hydrogen and hydroxyl groups are directed toward the observer, and so that the projections of the asymmetric carbon and adjacent carbons fall in a vertical line on the paper. By

[37] The *d* and *l* nomenclature is being considered at present by a Committee appointed by the Divisions of giological Chemistry, Chemical Education, and Sugar Chemistry of the American C hemical Society.

projecting the carbon, hydrogen, and hydroxyl groups to the plane of the paper, a formula is obtained in which the hydrogen and hydroxyl groups lie on opposite sides of the vertical line connecting the carbon atoms. The relation between the models and the projections is illustrated by the formulas for *d*- and *l*-glyceraldehydes.

If the molecule contains several asymmetric carbons they are projected on the paper in succession, keeping the carbon atoms in a vertical line with the reducing group uppermost, and turning the asymmetric carbon under consideration so that its hydrogen and hydroxyl groups are directed toward the observer before making the projection. The formula for the free aldehyde modification of *d*-glucose is represented below. If desired, the formula can be written horizontally with the reducing group on the right. The carbon atoms of the aldoses are numbered beginning with the reducing group, and of the

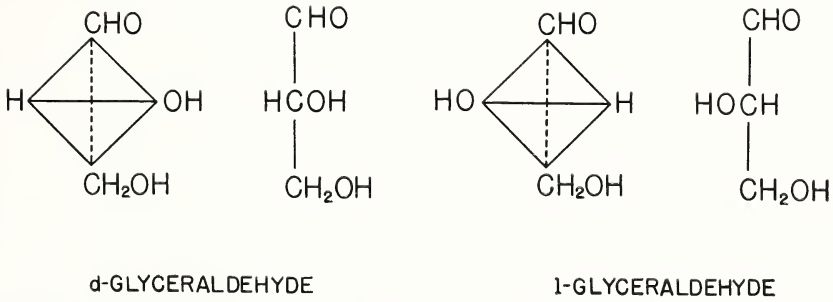
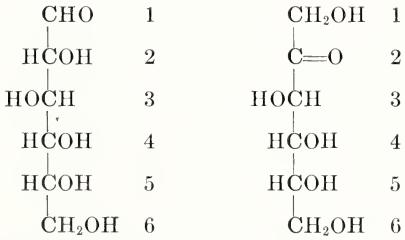


FIGURE 104.—*Relation between models and projectional formulas of d- and l-glyceraldehyde.*

ketoses beginning with the carbon on the end closer to the reducing group.



Aldehydo-d-glucose *Keto-d*-fructose

The investigations of Fischer [27] which established the configurations of carbons 2, 3, 4, and 5 in the simple sugars were based on the relationship of one sugar to another, and on the conversion of the sugars to alcohols, acids, and osazones. The latter products are open-chain compounds and consequently their study provided valid proofs for the structure of the open-chain modifications. When the open-chain compound is converted into a cyclic structure, free rotation about the carbon-carbon bonds is restricted and new structural problems arise.

Models for the ring modifications are obtained from the open-chain models by turning the various atoms about the carbon-carbon axes

in such manner that the hydroxyl on the fifth carbon for the pyranoses (and on the fourth carbon for the furanoses) is brought into contact and united with the carbonyl group. In the models representing the pryanoses, the atoms comprising the ring do not lie in a single plane, but form "Sachse" strainless ring structures. For representing the cyclic structures in print, modified Fischer projectional formulas are frequently employed, in which the lactol ring is drawn to the right or to the left according to the position of the hydroxyl involved in ring formation. These arbitrary formulas do not show the spatial relations as well as Haworth's hexagonal formulas [19], but the latter are more difficult to set in type. In the hexagonal formulas the hydrogen and hydroxyl groups are considered to lie above and below the plane of

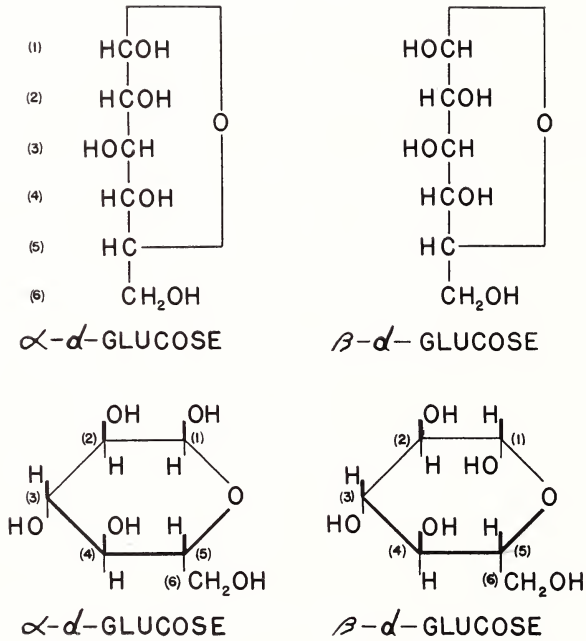


FIGURE 105.—*Fischer projectional and Haworth hexagonal formulas for d-glucose.*

the ring, when the edge of the ring which is printed in heavy type, is facing the observer.

The reducing carbon in the cyclic sugar is asymmetric and gives rise to two modifications, alpha and beta. The alpha and beta modifications depend upon whether the glycosidic hydroxyl lies on one side or the other of the lactonyl ring. When either form is dissolved in water, it undergoes spontaneously, at a measurable rate, intramolecular rearrangement whereby an equilibrium is established with the other modification. Since the two modifications usually exist in solution in dynamic equilibrium, the total sugar in solution can be separated in either form. By conductivity measurements in the presence of boric acid, Böeseken [28] proved that the glycosidic hydroxyl of α-*d*-glucose lies in the same direction as the hydroxyl of the second carbon, but on account of the tendency of the reducing sugars to

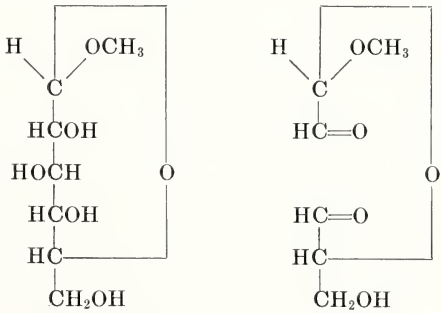
change from one form to another, for most sugars it is not possible to determine the configuration of the reducing group by direct methods. It is therefore necessary to assign structures for the alpha and beta sugars by indirect methods, such as by comparison with structurally related products.

If the hydrogen of the glycosidic hydroxyl is replaced by a methyl group, a product known as a methyl glycoside is obtained. In contrast to the free sugars, the glycosidic carbons in the glycosides do not rearrange in neutral and alkaline solutions. For this reason the configurations of the methyl glycosides can be determined by direct chemical methods. As mentioned on page 415, the investigations of Haworth and others have shown that the glycosides contain either five- or six-membered lactonyl rings, and that they are analogous to the alpha and beta furanose and pyranose sugars. Armstrong [29] showed by enzymic splitting that methyl *α-d*-glucoside yields *α-d*-glucose, and that methyl *β-d*-glucoside yields *β-d*-glucose. This proves that *α*- and *β-d*-glucose are analogous to the alpha and beta methyl *d*-glucosides. As noted by Simon [30], the optical rotations for *α*- and *β-d*-glucose and the methyl glucosides show the following relationship:

Methyl *α-d*-glucoside,	+155. 5	*α-d*-Glucose,	+106
Methyl *β-d*-glucoside,	− 31. 9	*β-d*-Glucose,	+ 22. 5
Mean	+61. 8	Mean	+64. 3

By extending this method of comparison the sugars can be correlated with the corresponding methyl glycosides, the ring structures and configurations of which have been determined experimentally.

A general method for ascertaining the configurations of the glycosides was developed by Jackson and Hudson [31]. This method depends on the reaction of the methyl glycosides with periodic acid, whereby the sugar ring is ruptured to give optically active diglycolic aldehydes, the configurations of which depend on the configurations of the first and ring-forming carbons of the parent glycoside. Thus, when methyl *α-d*-glucopyranoside (I) is treated with periodic acid, *D′*-methoxy-*D*-hydroxymethyl-diglycolic aldehyde [38] (II) is produced.



(I) Methyl *α-d*-glucopyranoside.

(II) *D′*-Methoxy-*D*-hydroxymethyl-diglycolic aldehyde.

[38] In conformity with the publication of Jackson and Hudson, capital *L* and *D* are used in these names to represent the configurations, rather than the small letters which are used elsewhere in this publication.

The same product was obtained from the alpha methyl pyranosides of glucose, mannose, galactose, and gulose. This proved that these substances have like configurations for carbons 1 and 5, and since the methoxyl of the glucoside lies to the right, as shown by the work of Böeseken [28], the methoxyls in the methyl α-*d*-galactosides, methyl α-*d*-mannosides, and methyl *a*-*d*-gulosides must also lie to the right. Application of the periodic acid oxidation to the beta pyranosides of the same sugars gives L'-methoxy-D-hydroxymethyl-diglycolic aldehyde, which proves that the glycosidic methoxyls lie to the left in these β-*d*-pyranosides. By essentially the same method the configurations of other glycosides can be ascertained.

Fortunately there is a close relationship between the configurations of the glycosides and their optical rotations. Insofar as our present knowledge is concerned, those glycosides which give D'-methoxy derivatives by oxidation with periodic acid are more dextrorotatory than the corresponding glycosides which give L'-methoxy derivatives. As brought out by the work of Hudson [32] in conjunction with the periodic acid oxidations [31], the contribution of the glycosidic carbon to the optical rotation is positive in those compounds in which the hydroxyl or methoxyl groups lie to the right when the formulas are written in the conventional manner. This relationship between configuration and optical rotation is useful in naming the alpha and beta modifications of the sugars and their derivatives.

4. NOMENCLATURE OF THE ALPHA AND BETA SUGARS

One of the most fundamental principles of stereochemical nomenclature is that the names of enantiomorphs differ merely in the prefix *d* or *l*. Thus the mirror image of α-*d*-glucose is called α-*l*-glucose. Since the absolute configurations of the glycosidic carbons in the two isomers are different, the absolute configuration cannot be used for the alpha and beta nomenclature. In order that the names of enantiomorphs be alike, in selecting the alpha-beta names it is necessary to consider the configuration of the glycosidic carbon in relation to some other group in the molecule, the configuration of which changes with the *d* and *l* classification. For a reference group, Hudson selected the terminal asymmetric carbon. This carbon is also used for the *d* and *l* classification in the Rosanoff system.

According to Hudson's nomenclature [33] the more dextrorotatory member of an alpha-beta pair in the *d*-series is designated as alpha, and if the substance belongs in the *l*-series, the more dextrorotatory member is called beta. Seemingly the optical rotations parallel the configurations. Freudenberg [34] has suggested that the alpha-beta names be based on configuration rather than on optical rotation. According to Freudenberg's system, substances of like configuration for the glycosidic and terminal asymmetric carbons are called alpha. If the configurations parallel the optical rotations, Freudenberg's and Hudson's classifications give the same names. In the normal aldohexoses, the hydroxyl, united with the terminal asymmetric carbon, forms the oxygen ring so that the configuration of this carbon atom is a characteristic feature of the ring. In the heptoses and higher sugars, the *d* and *l* classification depends on the configuration of the sixth or higher carbon which lies in the side chain and does not have anything to do with the configuration of the glycosidic carbon

For this reason, Hudson's and Freudenberg's alpha-beta names for the higher sugars do not result in a correlation of substances of like configuration for the groups comprising the pyranose ring.

Isbell [35, 36, 37] has pointed out the advantages of basing the alpha-beta names on the configuration of the ring-forming carbon, instead of the terminal carbon, and has suggested that *substances which have like configuration for the glycosidic and ring-forming carbons be called alpha, while substances which have unlike configuration for the glycosidic and ring-forming carbons be called beta.*[39]

In this publication the foregoing rule is followed for all substances in which the ring-forming carbon is asymmetric. *In case the ring-forming carbon is not asymmetric (as in the pentoses and ketohexoses), substances having like configurations for the glycosidic and terminal asymmetric carbons are called alpha, and those having unlike configurations are called beta.*

The alpha-beta classification, as used here, is based on configuration, but since the optical rotations seem to parallel the configurations, the alpha and beta names may be selected, at least provisionally, from the optical rotations by the following rule:

The more dextrorotatory member of the alpha-beta pair is called alpha if the ring-forming carbon has the *d* configuration, and beta if the ring-forming carbon has the *l* configuration. In case the ring-forming carbon is not asymmetric, the configuration of the terminal asymmetric carbon is used in selecting the name.

Fischer projectional formulas and the corresponding names are shown in figure 106 for the pentoses, hexoses, and heptoses. In the alpha isomers the projection of the glycosidic hydroxyl or other functional group falls at the point marked alpha; in the beta isomers the projection of the functional group falls at the point marked beta.

[39] A comparison of *d*-xylose, *d*-lyxose, *l*-arabinose, and *l*-ribose with *d*-glucose, *d*-mannose, *d*-galactose, and *a*-talose shows marked resemblance in the properties of each pentose and the configurationally related *d*-hexose [38]. For this reason, Isbell suggested naming the alpha and beta pyranose modifications of *d*-xylose, *d*-lyxose, *l*-arabinose, and *l*-ribose like the corresponding *d*-aldohexoses. In the ketose series, *d*-sorbose, *d*-tagatose, *l*-fructose, and *l*-psicose resemble the *d*-aldohexoses and might be classified likewise. The classification of the derivatives of *l*-arabinose and *l*-fructose with the closely related derivatives of *d*-galactose permits generalizations in regard to the reactions and properties of the alpha and beta sugars, but it involves changing the names for the derivatives of arabinose and fructose. Inasmuch as the alpha-beta nomenclature for the derivatives of arabinose and fructose most widely used at present is based on the configuration of the terminal asymmetric carbon, and since there appears to be a reluctance on the part of the workers in this field to change the names, in this publication the names for substances in which the ring-forming carbon is not asymmetric are based on the configuration of the *terminal* asymmetric carbon.

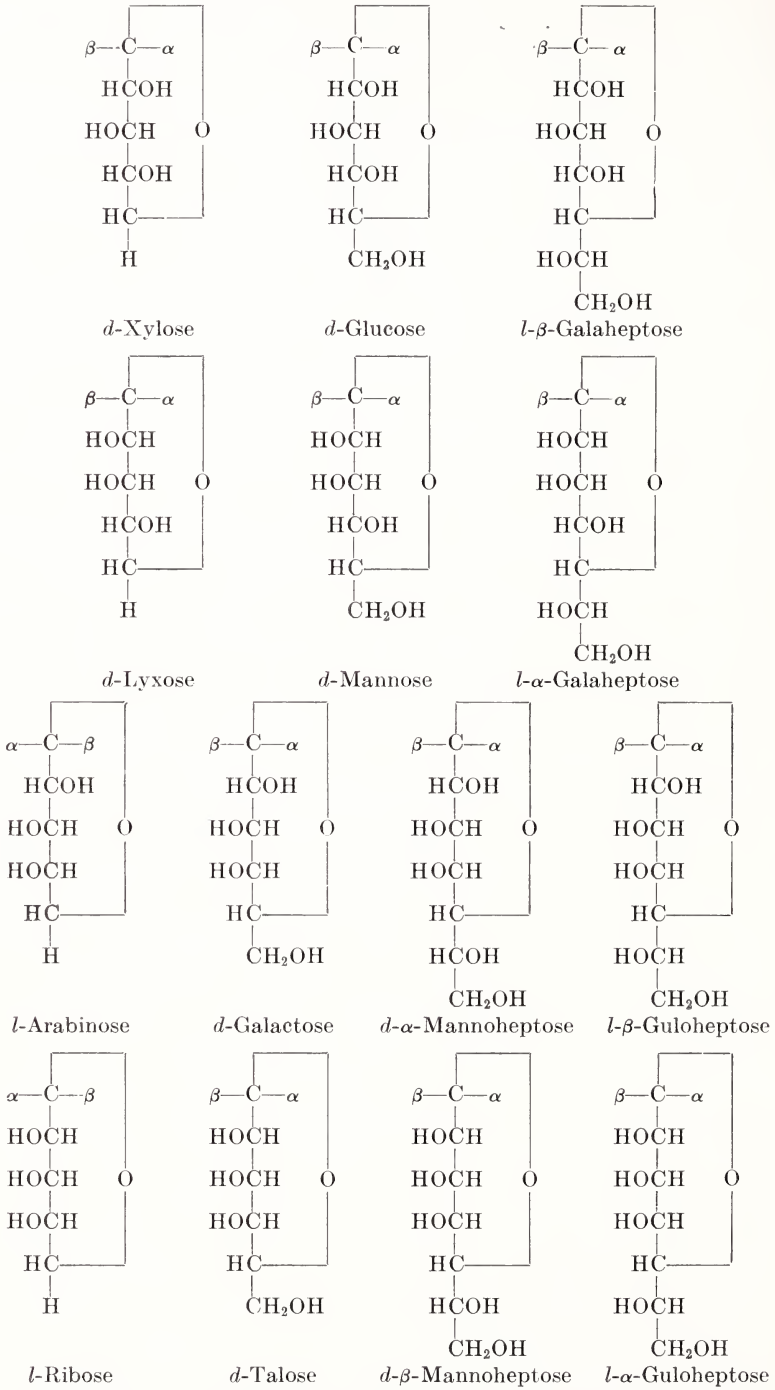
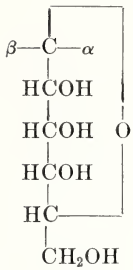
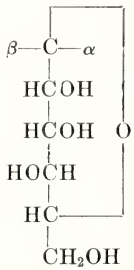


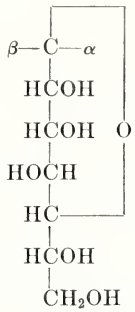
FIGURE 106.—*Fischer projectional formulas and the corresponding names for the pentoses, hexoses, and heptoses.*



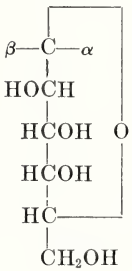
d-Allose



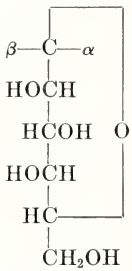
d-Gulose



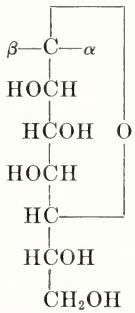
d-α-Glucoheptose



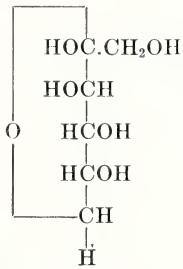
d-Altrose



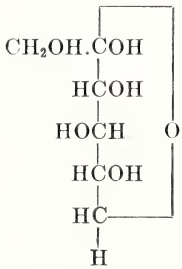
d-Idose



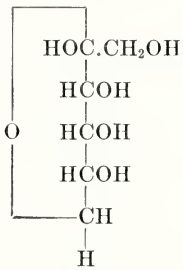
d-β-Glucoheptose



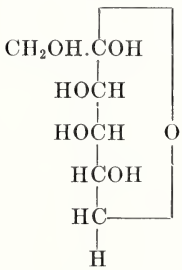
Levulose
β-*d*-Fructose



α-*d*-Sorbose



β-*d*-Psicose



α-*d*-Tagatose

FIGURE 106.—Continued

5. CORRELATIONS BETWEEN OPTICAL ROTATION AND STRUCTURE

Study of the relationship between structure and optical rotation began with Van't Hoff [39], who advanced the principle that the optical rotation of the molecule is equal to the algebraic sum of rotations due to the constituent atoms, the rotations of which change from $+A$ to $-A$ when the atomic configuration is replaced by its mirror image. Accordingly, Van't Hoff represented the optical rotations of the open-chain modifications of the four pentoses in the following manner:

No. 1	No. 2	No. 3	No. 4
$+A$	$+A$	$+A$	$-A$
$+B$	$+B$	$-B$	$+B$
$+C$	$-C$	$+C$	$+C$

"Since the sum of No. 2, No. 3, and No. 4 is equal to $A+B+C$, the rotation of arabinose (probably the highest) should be equal to the rotations of xylose, ribose, and the expected fourth type taken together." This concept, which is designated as the principle of optical superposition, has been applied to the sugars, sugar acetates, glycosides, and many sugar derivatives. Van't Hoff's fundamental principle may be valid provided the asymmetric carbon is replaced by its mirror image and no other changes follow. But each atom in the molecule influences the neighboring atoms, and consequently a stereoisomeric change results in a new distribution of atoms, electrons, and electromagnetic fields so that the conditions necessary for the valid application of the principle are not realized. The effect of changes in the configuration of neighboring groups on the optical rotation of an asymmetric carbon was noted by Rosanoff [40] and by Freudenberg and Kuhn [41]. The configurations of the atoms adjacent to a given asymmetric carbon appear to alter its optical rotation markedly, while the configurations of the atoms separated from the given asymmetric carbon appear to have less influence.

According to the principle of optical superposition, the optical rotation of the sugar is equal to the algebraic sum of the partial rotations at each of the asymmetric centers. For example, the molecular rotation of α-*d*-lyxose is represented by $A_{OH}-R_2-R_3+R_4$, where A_{OH}, R_2, R_3, and R_4 are the partial rotations at carbons 1, 2, 3, and 4. The optical rotations and configurations of the pentoses, hexoses, and heptoses are given in table 52.

TABLE 52.—*Optical rotation and configuration for the pyranose sugars*

Sugars	$[\alpha]_D^{20}$	Configuration						Molecular rotation
		C_1	C_2	C_3	C_4	C_5	C_6	
PENTOSES								
α-*d*-Lyxose	+5.6	+	−	−	+			+840
β-*d*-Lyxose	−72.6	−	−	−	+			−10,900
α-*d*-Xylose	+93.6	+	+	−	+			+14,050
β-*d*-Arabinose [1]	−190.6	−	−	+	+			−28,610
α-*d*-Arabinose.$CaCl_2.4H_2O$ [1]	−34.7	+	−	+	+			−11,560
α-*d*-Ribose [2]	−20.3	+	+	+	+			−3,050
METHYLPENTOSES								
α-*l*-Rhamnose.H_2O	−8.6	−	+	+	−	−		−1,570
β-*l*-Rhamnose	+38.4	+	+	+	−	−		+6,300
α-*l*-Fucose	−152.6	−	−	+	+	−		−25,050
α-*d*-Isorhamnose	+73.3	+	+	−	+	+		+12,030
HEXOSES								
α-*d*-Glucose	+112.2	+	+	−	+	+		+20,210
β-*d*-Glucose	+18.7	−	+	−	+	+		+3,370
α-*d*-Mannose	+29.3	+	−	−	+	+		+5,280
β-*d*-Mannose	−17.0	−	−	−	+	+		−3,060
α-*d*-Galactose	+150.7	+	+	−	−	+		+27,150
β-*d*-Galactose	+52.8	−	+	−	−	+		+9,510
α-*d*-Talose	+68.0	+	−	−	−	+		+12,250
β-*d*-Talose	+13.2	−	−	−	−	+		+2,380
α-*d*-Gulose.$CaCl_2.H_2O$	+37.1	+	+	+	−	+		+11,470
β-*d*-Allose [2]	−0.2	−	+	+	+	+		−40
β-*d*-Altrose [2]	+32.6	−	−	+	+	+		+5,900
HEPTOSES								
α-*d*-α-Galaheptose.H_2O	−25.2	−	+	+	−	−	+	−5,750
β-*d*-β-Galaheptose	−19.2	+	−	+	−	−	+	−4,040
α-*d*-α-Guloheptose	−45.7	−	+	+	+	−	+	−9,610
α-*d*-β-Guloheptose	−120.5	−	−	+	+	−	+	−25,330
β-*d*-α-Glucoheptose	−28.7	−	+	+	−	+	+	−6,030
β-*d*-β-Glucoheptose [2]	−0.1	−	−	+	−	+	+	−20
α-*d*-α-Mannoheptose.H_2O	+120.0	+	+	−	−	+	+	+27,380
β-*d*-α-Mannoheptose.H_2O	+42.3	−	+	−	−	+	+	+9,650
α-*d*-β-Mannoheptose.H_2O	+45.7	+	−	−	−	+	+	+10,430

[1] Values obtained from enantiomorphic isomer.
[2] Configuration questionable.

The value for twice the rotation ($2R$) of an asymmetric carbon, perhaps better called the rotational difference, may be obtained by subtracting the equations representing the optical rotations of the separate sugars in such a manner as to eliminate all of the variables except one. Some values calculated in this manner are given in table 53. In order to bring out relations between the various values for the rotational differences and the configurations of the neighboring groups, the configurations of the contiguous groups are indicated by the symbols given in the column on the right. The first term in the symbol represents the configuration of the carbon which lies above the one under consideration, when the formula is written with the reducing group uppermost, while the second term represents the configuration of the carbon which lies below.

323414°—42——29

The rotational difference corresponding to the first, or reducing carbon, has been designated $2A_{OH}$ in accord with the terminology originated by Hudson. The numerical values for $2A_{OH}$ obtained from the alpha and beta modifications of arabinose, glucose, and galactose, and other sugars having like configurations for carbons 2 and 5, are approximately 17,000, while the values from the rotations of mannose and talose, and other sugars having unlike configurations for carbons 2 and 5, are considerably lower, approximately 10,000.

TABLE 53.—*Differences in molecular rotation (principle of optical superposition)*

Molecular rotations	Rotational difference		Configuration of adjacent groups
l-Arabinose (+28,610)−*l*-arabinose $CaCl_2.4H_2O$ (+11,560)	$2A_{OH}$	+17,050	[1] 0, +
α-*d*-Glucose (+20,210)−β-*d*-glucose (+3,370)	$2A_{OH}$	+16,840	*d*, +
α-*d*-Galactose (+27,150)−β-*d*-galactose (+9,510)	$2A_{OH}$	+17,640	*d*, +
α-*d*-α-Mannoheptose (+27,380)−β-*d*-α-mannoheptose (+9,650)	$2A_{OH}$	+17,730	*d*, +
α-Lactose (+30,630)−β-lactose (+11,950)	$2A_{OH}$	+18,680	*d*, +
α-*d*-Lyxose (+840)−β-*d*-lyxose (−10,900)	$2A_{OH}$	+11,740	0, −
α-*d*-Mannose (+5,280)−β-*d*-mannose (−3,060)	$2A_{OH}$	+8,340	*d*, −
α-*d*-Talose (+12,250)−β-*d*-talose (+2,380)	$2A_{OH}$	+9,870	*d*, −
α-[4-Glucosido-mannose] (+5,300)−β-[4-glucosido-mannose] (−2,200)	$2A_{OH}$	+7,560	*d*, −
α-*d*-Rhamnose (+1,570)−β-*d*-rhamnose (−6,300)	$2A_{OH}$	+7,870	*d*, −
α-*d*-Xylose (+14,050)−α-*d*-lyxose (+840)	$2R_2$	+13,210	α, −
α-*d*-Glucose (+20,210)−α-*d*-mannose (+5,280)	$2R_2$	+14,930	α, −
α-*d*-Galactose (+27,150)−α-*d*-talose (+12,250)	$2R_2$	+14,900	α, −
α-*l*-β-Guloheptose (+25,330)−α-*l*-α-guloheptose (+9,610)	$2R_2$	+15,720	α, −
α-*d*-α-Mannoheptose (+27,380)−α-*d*-β-mannoheptose (+10,430)	$2R_2$	+16,950	α, −
β-*d*-Allose (−40)−β-*d*-altrose (+5,900)	$2R_2$	−5,940	β, +
β-*d*-α-Glucoheptose (−6,030)−β-*d*-β-glucoheptose (−20)	$2R_2$	−6,010	β, +
β-*d*-Glucose (+3,370)−β-*d*-mannose (−3,060)	$2R_2$	+6,430	β, −
β-*d*-Galactose (+9,510)−β-*d*-talose (+2,380)	$2R_2$	+7,130	β, −
l-Arabinose (+11,560)−*l*-ribose (+3,050)	$2R_2$	+8,510	[2] β, −
β-Cellobiose (+4,860)−β-4-glucosido-mannose (−2,200)	$2R_2$	+7,060	β, −
β-*d*-Allose (−40)−β-*d*-Glucose (+3,370)	$2R_3$	−3,410	+, +
α-*d*-Gulose (+11,470)−α-*d*-Galactose (+27,150)	$2R_3$	−15,680	+, −
β-*d*-α-Glucoheptose (−6,030)−β-*d*-α-Mannoheptose (+9,650)	$2R_3$	−15,680	+, −
β-*d*-Altrose (+5,900)+β-*d*-mannose (−3,060)	$2R_3$	+8,960	−, +
β-Celtrobiose (+4,900)−β-4-glucosido-mannose (−2,200)	$2R_3$	+7,100	−, +
α-*d*-Xylose (+14,050)−β-*l*-arabinose (+28,610)	$2R_4$	−14,560	−, 0
β-*d*-Lyxose (−10,900)−*l*-ribose (+3,050)	$2R_4$	−13,950	−, 0
α-*d*-Glucose (+20,210)−α-*d*-galactose (+27,150)	$2R_4$	−6,940	−, +
β-*d*-Glucose (+3,370)−β-*d*-galactose (+9,510)	$2R_4$	−6,140	−, +
α-*d*-Mannose (+5,280)−α-*d*-talose (+12,250)	$2R_4$	−6,970	−, +
β-*d*-Mannose (−3,060)−β-*d*-talose (+2,380)	$2R_4$	−5,440	−, +
α-*l*-α-Galaheptose (+5,750)−α-*l*-α-guloheptose (+9,610)	$2R_4$	−3,860	−, +
β-*d*-Mannose (−3,060)−α-*l*-gulose (−11,470)	$2R_5$	+8,410	*Trans* [1]
β-*d*-Allose (−40)−α-*l*-talose (−12,250)	$2R_5$	+12,210	*Trans* [1]
α-*d*-Galactose (+27,150)−β-*l*-altrose (−5,900)	$2R_5$	+33,050	*Trans* [1]
α-*l*-α-Galaheptose (+5,750)−β-*l*-α-glucoheptose (+6,030)	$2R_5$	−280	*Cis* [1]
α-*d*-α-Mannoheptose (+27,380)−α-*l*-β-guloheptose (+25,330)	$2R_6$	+2,050	+, 0
α-*d*-β-Mannoheptose (+10,430)−α-*l*-α-guloheptose (+9,610)	$2R_6$	+820	+, 0

[1] Hydroxyls on carbons 1 and 4 are *cis* or *trans*, as indicated.
[2] Carbon 1 in α-*l*-arabinose and in α-*l*-ribose (Hudson's nomenclature) has the same configuration as carbon 1 in the β-*d*-aldohexoses. See footnote 39.

The difference in the optical rotations of two sugars of diverse configuration for carbon 2 gives $2R_2$, a value which has been called the "epimeric difference" [42]. The optical rotation of an asymmetric carbon which lies between two asymmetric groups is influenced by the configurations of both groups [43]. There are four arrangements or combinations involving the configurations of the carbons which lie on either side of carbon 2. These are represented symbolically in the following manner: (1) α, +; (2) α, −; (3) β, +; (4) β, −. Epimeric

pairs corresponding to the first group are not known products at present but would be represented by α-*d*-gulose and α-*d*-idose, or by α-*d*-allose and α-*d*-altrose. In the hexose series the second group is represented by α-*d*-glucose and α-*d*-mannose, and by α-*d*-galactose and α-*d*-talose. The epimeric differences obtained from these pairs, +14,930 and +14,900, are in excellent agreement. The third group is represented by β-*d*-allose and β-*d*-altrose, and by β-*d*-α-glucoheptose and β-*d*-β-glucoheptose. The epimeric differences for these pairs are −5,940 and −6,010. Since these sugars have not been extensively studied, it is quite possible that β-*d*-altrose or β-*d*-β-glucoheptose may be improperly classified. The fourth group is represented in the hexose series by β-*d*-glucose and β-*d*-mannose, and by β-*d*-galactose and β-*d*-talose. The epimeric differences obtained from these pairs are +6,430 and +7,130. The epimeric differences obtained for various configurations bring out the need for considering the configuration of adjacent groups in making comparisons, and emphasize the complex character of the problem.

The rotational differences for carbon 3, obtained from sugars which represent three possible combinations for the configurations of the adjacent groups, give values of approximately −16,000, −3,000, and +8,000. The differences in these values show that the configurations of the adjacent carbons influence rotation. Data are not available for calculating the rotational differences for the fourth group. For two of the configurations, the comparisons give results in approximate agreement with one another.

The data available for calculating the rotational differences for carbon 4 in the hexose series are limited to only one combination for the configurations of the adjacent carbon atoms. Four calculations from the optical rotations of eight sugars give values in approximate agreement with each other, namely, −6,940, −6,140, −6,970, and −5,440. These values are in accord with those obtained in the heptose series for substances of like configuration, but they are not strictly comparable with those obtained from the pentoses, because the pentoses differ from the hexoses and heptoses in the substituent group on adjacent carbon 5.

The determination of the optical rotation of carbon 5 is complicated, because any change in its configuration affects the adjacent ring oxygen, which in turn determines the alpha and beta positions of the first carbon. Consequently, the rotational differences for carbon 5 ($2R_5$) include any changes which may be induced by the dissymmetry of the molecule as a whole. The data at hand are not sufficient to evaluate this factor. The comparisons involving the optical rotations of allose and altrose do not appear to be in accord. The discrepancy may be caused by improper classification, erroneous optical rotations, or unknown structural differences, such as differences in the conformation of the rings.

The rotational differences clearly show that optical rotation is not uniformly an additive property and that dissimilarity in the configurations of the contiguous atoms results in deviations from the Van't Hoff theory of optical superposition. The work of Tschugaeff, Kuhn, Lowry, and others [24, p. 429] shows that each asymmetric carbon in an optically active substance gives rise to one or more partial rotations, which may be correlated with absorption bands of characteristic frequency having their origin in particular electronic transitions

taking place in the molecule. These transitions are not influenced greatly by atoms or groups at some distance from the asymmetric carbon but are influenced by the neighboring groups. The optical rotation in the visible spectrum is chiefly governed by the absorption bands nearest the wave length used for the rotation measurements. Since the bands are not located at the same wave lengths for all sugars, the partial rotation varies in irregular fashion with the wave length. For this reason the difference in the rotations of two sugars depends in part on the light used for making comparison, and it is obvious that the optical rotations cannot be rigorously represented by the simple algebraic equations suggested by Van't Hoff.

Nevertheless, the active part that the principle of optical superposition has played in the development of carbohydrate chemistry is sufficient justification for continuing its use. It has been amply demonstrated that substances of similar *structure and configuration* give approximately like rotational differences.

For correlating optical rotation and structure, Hudson [32] has noted a number of approximations which are expressed in several empirical rules. The so-called first rule of isorotation relates to the optical rotation of the glycosidic carbon. If the formulas for alpha and beta glucose are written as ring structures differing solely in the configuration of carbon 1, and if the rotation due to the end asymmetric carbon is A, and the rotation due to the rest of the molecule is B, the molecular rotation of one isomer will be $+A+B$, and the rotation of the other isomer will be $-A+B$. The sum of the rotations is $+2B$ and their difference $+2A$. When the molecular rotations of the alpha and beta modifications of glucose, galactose, and lactose are compared on the one hand, and the molecular rotations of lyxose, rhamnose, mannose, and 4-glucosidomannose are compared on the other hand, it will be observed that the differences in the molecular rotations for the alpha-beta pairs in each group are nearly constant. The members of the first group have the configuration H—C—OH for the carbon adjacent to the glycosidic group, while the members of the second group have the configuration HO—C—H. Many similar comparisons reveal that the rotational difference, $2A$, is nearly constant for substances which have like glycosidic groups, like ring structures, and like configurations on the adjacent carbon atoms. This approximate equality is the basis of the first rule of isorotation which states that *the rotation of the glycosidic group is affected in only a minor degree by changes in the structure of the remainder of the molecule provided the changes are not on the contiguous atoms.*[40]

Hudson's second rule of isorotation relates to the optical rotation of the rest of the molecule. The sum of the molecular rotations of the alpha and beta sugars, $+2B$, varies from sugar to sugar, but if the sums of the molecular rotations of the sugars are compared with the sums of the molecular rotations of the methyl glycosides, it will be observed that the values of $2B$ obtained for the sugars are in close agreement with the values of $2B'$ obtained for the glycosides. This is the basis for the second rule of isorotation which states that *changes in the structure of the glycosidic carbon affect in only a minor degree the rotation of the remainder of the molecule.* As may be observed from data given in table 54, the values for $2B$ are in approximate agreement

[40] Hudson's original rule does not exclude changes on the contiguous atoms.

for substances which do not have large differences in the glycosidic group.

TABLE 54.—*Sum of the molecular rotations (2B) for some alpha and beta derivatives of d-glucose*

Glycosidic group	[M] Alpha form	[M] Beta form	Sum 2B	Glycosidic group	[M] Alpha form	[M] Beta form	Sum 2B
-OH	+20, 210	+3, 370	+23, 580	$-OC_3H_5$ (allyl)	+29, 010	−9, 320	+19, 690
$-OCH_3$	+30, 860	−6, 640	+24, 220	$-OCH_2CH_2(OH)$	+30, 380	−6, 850	+23, 530
$-OC_2H_5$	+31, 360	−6, 950	+24, 410	$-OCH_2C_6H_5$	+35, 410	−15, 020	+20, 390
$-OC_3H_7$	+31, 290	−7, 760	+23, 530	$-OC_6H_5$	+46, 330	−18, 190	+28, 140

The value of 2B obtained for the alpha and beta phenyl glucosides (+28,140) differs considerably from the value (+24,220) obtained for the alpha and beta methyl glucosides and related substances. The introduction of an unsaturated chromophoric group appears to induce a change in the optical rotation of the rest of the molecule. The chromophoric group is particularly influential when adjacent to the asymmetric center. Its influence is small when it is at some distance from the asymmetric center, as for example, in the benzylglucosides. As may be observed from the data given in table 55, the sums for the molecular rotations of the alpha and beta sugars do not differ widely from the sums for the molecular rotations of the corresponding methyl glycosides.

TABLE 55.—*Sums of the rotations of the alpha and beta sugars in comparison with those of the α- and β-methyl glycosides (second rule of isorotation)*

Substance	Sum of the molecular rotations of—		Substance	Sum of the molecular rotations of—	
	α-Sugar+ β-Sugar	α-Methyl pyranoside+ β-Methyl pyranoside		α-Sugar+ β-Sugar	α-Methyl pyranoside+ β-Methyl pyranoside
d-Xylose	[1] +11, 050	+14, 510	*d*-Glucose	+23, 580	+24, 220
d-Lyxose	−10, 060	−11, 280	*d*-Mannose	+2, 220	+1, 830
l-Arabinose	+40, 170	+43, 140	*d*-Galactose	+36, 660	+38, 050

[1] The value for the rotation of β-*d*-xylose was taken from Hudson's indirect measurements by means of solubility experiments.

The accumulation of a large amount of experimental data has brought out other approximations which are useful for correlating optical rotation and structure. One of the most obvious is the striking similarity in the optical rotations of substances which have like configurations for the carbon atoms comprising the pyranose ring. This generalization can be expressed in a rule which states that *changes in the side chains attached to the pyranose ring affect in only a minor degree the rotation of the remainder of the molecule.* The optical rotations of a few sugar derivatives, which differ merely in the groups attached to the pyranose ring, are given in table 56.

As might be anticipated from the close similarity in structure, the molecular rotations of the configurationally related hexoses and heptoses resemble one another more closely than they resemble the rotations of the configurationally related pentoses and methyl pen-

toses. A number of unexplained variations may be noted in table 56; these call for further investigation to ascertain whether they arise from errors or from unknown differences in structure.

TABLE 56.—*Molecular rotation of substances of like configuration of the pyranose ring*

Configuration of pyranose ring	Substituent group on carbon 5				
	$-H$ (Pentose)	$-CH_3$ (Methyl pentose)	$-CH_2OH$ (Hexose)	$-\overset{H}{\underset{OH}{C}}-CH_2OH$ (Heptose)	$-\overset{OH}{\underset{H}{C}}-CH_2OH$ (Heptose)
SUGARS					
α-*d*-Glucose (α+−++)	+14, 050	+12, 030	+20, 210		
β-*d*-Glucose (β+−++)			+3, 370	+4, 040	
α-*d*-Mannose (α−−++)	+840	+1, 570	+5, 280	+5, 750	
β-*d*-Mannose (β−−++)	−10, 900	−6, 300	−3, 060		
α-*d*-Galactose (α+−−+)	+28, 610	+25, 050	+27, 150	+25, 330	+27, 380
β-*d*-Galactose (β+−−+)	+11, 560		+9, 510		+9, 650
α-*d*-Talose (α−−−+)			+12, 250	+9, 610	+10, 430
β-*d*-Talose (β−−−+)	+3, 050		+2, 380		
METHYL GLYCOSIDES					
α-*d*-Glucose (α+−++)	+25, 260		+30, 860	+24, 200	
β-*d*-Glucose (β+−++)	−10, 750	−9, 820	−6, 640	−8, 100	
α-*d*-Mannose (α−−++)	+9, 750	+11, 140	+15, 380	+15, 700	
β-*d*-Mannose (β−−++)	−21, 030	−17, 000	−13, 550		
α-*d*-Galactose (α+−−+)	+40, 300	+35, 100	+38, 180		
β-*d*-Galactose (β+−−+)	+2, 840	−2, 900	0		
ACETYLATED SUGARS					
α-*d*-Glucose (α+−++)	+28, 400		+39, 700	+25, 800	
β-*d*-Glucose (β+−++)	−7, 860		+1, 480	−14, 000	
α-*d*-Mannose (α−−++)	+8, 000		+21, 470		
β-*d*-Mannose (β−−++)		−4, 620	−9, 840		
α-*d*-Galactose (α+−−+)	+46, 800	+39, 900	+41, 650		+55, 860
β-*d*-Galactose (β+−−+)	+13, 500		+9, 760		+15, 770

Several relationships connecting the optical rotations and configurations of the sugar acids and their derivatives have been noted. The first of these is the Hudson lactone rule [44, 45], which states that lactones, in which the oxygen ring lies to the right when the projectional formulas are written in the conventional manner, are more dextrorotatory than the parent acids, and if the oxygen ring lies on the left, the lactone is the more levorotatory. The rule was originally derived from the optical rotations of gamma lactones, but it appears to apply equally well to the delta lactones. With the exception of allonic, manno-nononic, and digitoxonic lactones, the sign of rotation in water solution corresponds with the configuration of the ring-forming carbon. That is, lactones in which the oxygen ring lies to the right are usually dextrorotatory, while lactones in which the oxygen ring lies to the left are usually levorotatory. Levene [46, 47] and also Hudson [48] have pointed out that the phenylhydrazides and amides of the aldonic acids are dextrorotatory when the hydroxyl on the alpha carbon lies to the right. These relationships are very useful for determining the structures of new acids formed by extending the carbon chain, because frequently the phenylhydrazides and amides

are used for separating the products. Levene [46, 47] has shown that the alkali salts of the aldonic acids are more dextrorotatory than the free acids when the hydroxyl on the alpha carbon lies to the right, and Isbell [49] has shown that the lead salts are more levorotatory than the alkaline earth salts when the hydroxyl on the alpha carbon lies to the right. These empirical rules make the classification of newly prepared sugar acids a very simple matter.

TABLE 57.—*Molecular rotation of the aldonic acids and related products*

Substance	Acid	γ-Lactone	Amide	Phenylhydrazide	Configuration				
					C_2	C_3	C_4	C_5	C_6
d-Xylonic	----------	+13,600	+7,350	----------	+	−	+		
d-Isorhamnonic	----------	+10,850	----------	----------	+	−	+	+	
d-Gluconic	−1,350	+12,110	+6,090	+3,440	+	−	+	+	
l-β-Galaheptonic [1]	----------	----------	+4,500	+2,500	+	−	+	+	−
d-Lyxonic	+1,100	+12,070	----------	----------	−	−	+		
d-Rhamnonic [1]	----------	+6,360	−4,960	−4,650	−	−	+	+	
d-Mannonic	----------	+9,170	−3,380	−2,320	−	−	+	+	
l-α-Galaheptonic [1]	−570	+10,900	−3,220	−2,700	−	−	+	+	−
l-Arabonic	−1,630	−10,600	+6,190	+3,560 [1]	+	−	−		
d-Fuconic [1]	----------	−12,700	+5,570	----------	+	−	−	+	
d-Galactonic	−2,670	−13,790	+6,210	+2,980	+	−	−	+	
l-β-Guloheptonic [1]	−2,900	----------	----------	+4,870	+	−	−	+	−
d-α-Mannoheptonic	----------	−15,450	+6,310	+6,600	+	−	−	+	+
l-Ribonic	+2,920	−2,660	−2,710	----------	−	−	−		
d-Talonic	+3,990	−6,180	−2,560	−7,270	−	−	−	+	
d-β-Mannoheptonic	+900	−7,430	----------	−8,160	−	−	−	+	+
l-α-Guloheptonic [1]	+2,850	−5,310	----------	−9,270	−	−	−	+	−
d-Gulonic	----------	−10,170	+3,140	----------	+	+	−	+	
d-α-Glucoheptonic	−1,970	−11,660	+2,390	+2,940	+	+	−	+	+
d-β-Glucoheptonic	+300	−17,100	−6,800	----------	−	+	−	+	+
d-Allonic acid	----------	−1,100 [1]	----------	+7,410	+	+	+	+	
d-Altronic acid [1]	+1,600	----------	----------	−5,300	−	+	+	+	

[1] Value derived from the enantiomorph by reversing the sign of the rotation.

The marked parallelism between the optical rotations and configurations which has been considered briefly is but one of many correlations which exist between the properties and the configurations of the sugars and their derivatives. In the next section, some of the chemical properties will be considered in relation to structure and configuration.

6. CORRELATIONS BETWEEN THE CONFIGURATIONS AND THE CHEMICAL PROPERTIES OF THE SUGARS

The alpha and beta sugars have diverse configurations for their reducing carbons and marked differences have been found in their properties. An extensive investigation of the alpha and beta sugars was initiated by Isbell, who sought to determine the effect of configuration on the relative reactivity of the alpha and beta sugars. Some of the data obtained in this investigation are given in table 58, from which it may be observed that the beta sugars are oxidized by bromine water more rapidly than the corresponding alpha sugars.

TABLE 58.—*Rates of oxidation of alpha and beta sugars* [35, 36, 37]

[In aqueous solutions at 0° C containing 0.05 mole of sugar, and approximately 0.08 mole of free bromine per liter and buffered with barium carbonate and carbon dioxide]

Sugar	Relative reaction rates $\frac{k_{sugar}}{k_{\alpha\text{-}d\text{-glucose}}}$		k_β/k_α	Less reactive fraction in equilibrium solution
	Alpha form (*cis*)	Beta form (*trans*)		
				Percent
d-Glucose	1.0	39	39	37
d-Mannose	1.6	24	15	69
d-Galactose	1.3	50	38	31
d-Gulose	2.2	13	6	18
d-Talose	2.4	26	11	56
d-Xylose	2.8	52	19	32
d-Lyxose	4.9	14	3	80
l-Arabinose[1]	3.0	52	18	32
l-Ribose[1]	6.1	45.5	8	89
d-β-Galaheptose	0.8	53	66	37
d-α-Galaheptose	2.3	56	25	79
d-α-Mannoheptose	1.3	58	46	33
d-β-Guloheptose	1.1	56	52	37
d-α-Glucoheptose	1.4	12	9	12
d-β-Glucoheptose	0.9	11	12	22
l-Rhamnose	2.8	24	9	69
Lactose	0.9	30	33	38
Maltose	.8	48	64	38

[1] Isbell's original nomenclature.

In many reactions the arrangement of the hydroxyls in relation to the plane of the ring is an especially important factor in influencing the rate and course of the reaction. Condensations in which two hydroxyls combine with another group take place when the hydroxyls lie on the same side of the ring. Thus the behavior of the sugars and their derivatives in their reactions with acetone, benzaldehyde, boric acid, and many other substances is largely conditioned by the *cis* or *trans* arrangement of the hydroxyl groups [50, 51, 28]. The facility with which boric acid combines with *cis*-hydroxyls on adjacent atoms was mentioned with respect to the structure of alpha and beta glucose (p. 422). The property of increasing the electrical conductivity of boric acid appears to be characteristic of all sugars which have two hydroxyl groups on adjacent carbon atoms on the same side of the ring. Normally, condensation with acetone involves *cis*-hydroxyl groups on adjacent carbon atoms, making a cyclic link of five atoms [52], while condensation with benzaldehyde usually involves alternate *cis*-hydroxyls, making a cyclic link of six atoms [53].

In the presence of acid catalysts the free sugars react in the furanose or the pyranose form, depending upon which form is the more favorable for the condensation reaction. Thus glucose forms a 1,2-3,5-diacetone derivative, even though the free sugar exists in the pyranose modification. Correlations have been made also between the *cis-trans* configurations and the tendency to form anhydrosugars and sugar anhydrides. Thus α-*d*-glucose yields a glucosan by condensation between the hydroxyls of carbons 1 and 2; β-*d*-glucose, however, yields a glucosan by condensation between the hydroxyls of carbons 1 and 6 [54]. Apparently the configuration of carbon 1 determines the nature of the product formed. The importance of *cis-trans* configura-

tional relationships in the formation of anhydrosugars and orthoacetates was reviewed recently by Isbell [55], who suggested that many carbohydrate reactions can be explained by Werner's concept [56] for the Walden inversion. Intramolecular condensation reactions involving Walden inversion appear to take place only on the side of the carbon opposite the departing group.

The influence of the *cis-trans* configuration of the sugars and their derivatives in relation to their biological behavior has been recognized for a long time. The sorbose bacterium, for example, oxidizes sugar alcohols to ketoses when they contain the grouping, $-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_2OH$, with the CH(OH) groups having a *cis* configuration in the projectional formula [57]. The relationship between *cis-trans* configuration and rates of enzyme action has also been studied [58].

Even though many generalizations can be reached by considering only certain aspects of the molecule, each group influences to some extent the properties of the others, and therefore it is essential to consider also the configuration of the molecule as a whole. In the pyranoses, the carbon and ring oxygen atoms are tied up in a ring and cannot exhibit free rotation; consequently the pyranose ring forms a fundamental structure about which the hydroxyls and hydrogens are distributed according to the configurations of the constituent carbon atoms. The arrangement of the groups on either side of the ring makes up the thickness and general conformation of the molecule. The different configurations for the 5 asymmetric carbon atoms of the ring give rise to 32 isomeric pyranoses, which consist of 16 pairs of enantiomorphs. These fundamental configurational types are represented by the alpha and beta modifications of glucose, mannose, galactose, talose, gulose, idose, allose, and altrose and are illustrated by the formulas on p. 426. By substitution, all pyranose sugars are derived from these fundamental types, or from their enantiomorphs. The aldopentoses, methylpentoses, and heptoses differ from the aldohexoses in that the CH_2OH group of the latter is replaced by hydrogen, the methyl group, or by the $CHOH.CH_2OH$ group, respectively. The ketoses differ from the aldoses in that the H on the first carbon of the aldose is replaced by a CH_2OH group. If the sugars are considered in this manner, sorbose, xylose, β-galaheptose, maltose, lactose, and cellobiose are merely substituted glucoses, or levulose, perseulose, arabinose, α-mannoheptose, and β-guloheptose are merely substituted galactoses.

The tendency of a sugar or a sugar derivative to form five- or six-membered lactol rings is dependent on the character of the substituent groups, and on the configuration of the carbon atoms involved in forming the furanose and pyranose rings. This subject will be considered more fully in the next chapter.

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XXIX. MUTAROTATION AND SUGARS IN SOLUTION

1. CHARACTERISTICS OF THE EQUILIBRIUM STATE

Dubrunfaut [1] discovered that when glucose is dissolved in water, the optical rotatory power of the solution decreases on standing until finally it reaches a constant value. Subsequently, Pasteur [2], Erdmann [3], and others [4] found that the optical rotations of freshly prepared solutions of the reducing sugars in general change on standing, a phenomenon which came to be known as *mutarotation.*

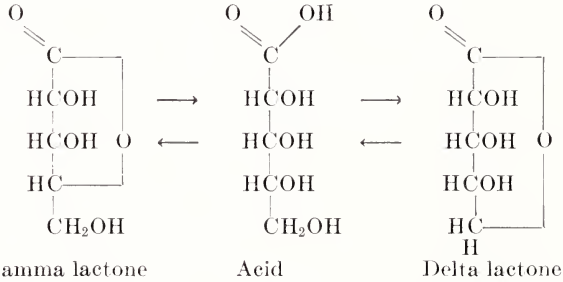
In 1846, when Dubrunfaut discovered mutarotation, he advanced the hypothesis that the change in optical rotation is caused by a change in molecular structure. After many years this hypothesis was confirmed by Tanret's preparation [5] of two forms of glucose and lactose, one having a higher rotation than the stable solution and the other having a lower rotation. Fischer's preparation of two methyl glucosides and Armstrong's discovery [6] that on enzymic hydrolysis the more dextrorotatory glucoside yields a sugar solution with a rotatory power greater than the equilibrium value and that the less dextrorotatory glucoside yields a sugar solution with a rotatory power less than the equilibrium value furnished a clue as to the character of the change involved in the mutarotation reaction. Subsequent work has shown that the mutarotation reactions consist in the reversible interconversion of the various modifications of the sugars and that many mutarotation reactions are caused almost entirely by the interconversion of the alpha and beta pyranose modifications. Since the several modifications in the sugar solution have different physical properties, the mutarotation reaction may be followed by the changes in solubility, volume, refractivity, and energy, in addition to the optical rotations.

As mentioned on page 414, the equilibrium involves the structures found in the open-chain sugar, the alpha and beta pyranose modifications, and the alpha and beta furanose modifications. The relative proportions of these constituents vary greatly from sugar to sugar and with the experimental conditions. The separation of numerous open-chain derivatives is evidence for the presence of the open-chain modification, but the lack of strong characteristic aldehydo reactions indicates that the open-chain modification is not present in large quantity. In weakly alkaline solution some sugars show a faint absorption band in the region characteristic of the carbonyl group [7]. This absorption band is further evidence that the open-chain modification is present only in small quantity. The ease with which the alpha and beta pyranose modifications can be crystallized shows that they are the predominating constituents of the sugar solution. For alpha and beta furanoses there are no characteristic qualitative tests such as the absorption band of the open-chain modification. The preparation of the methyl furanosides and other furanose derivatives and the crystallization of a calcium chloride compound of a manno-furanose [8, 9] imply that the furanoses are present. This inference is further substantiated by the complex mutarotation reactions, and by the similarity of the mutarotation of levulose to the mutarotation of the furanose form of levulose liberated from sucrose by invertase [10].

The position of the equilibrium between the various modifications in sugar solutions appears to depend upon the configuration of the

sugar and upon the substituent groups. Aldoses which have the glucose, mannose, and gulose structures establish equilibrium states consisting almost exclusively of the alpha and beta pyranose modifications [11]. Aldoses which have the galactose, talose, and idose structures establish equilibrium states containing small but substantial quantities of the furanose modifications and larger quantities of the alpha and beta pyranose modifications [12, 13, 14, 15]. Sugars which have the fructose structure establish equilibrium states consisting for the most part of a single pyranose modification with a substantial proportion of a furanose modification [10], and sugars which have the allose, altrose, sorbose, and tagatose structures establish equilibrium states consisting largely of a single pyranose modification [16, 17, 18, 19]. Replacing the hydrogen of the aldehydo group by a CH_2OH group to give a ketose results in a large alteration in the equilibrium proportions of the various ring and open-chain modifications of the resulting sugar. Isbell and Pigman [10] have shown that an equilibrium solution of levulose does not contain an appreciable quantity of the beta pyranose modification, even though the equilibrium solution of the structurally related aldose (*d*-arabinose) contains 73 percent of the beta pyranose modification. Furthermore, the proportions for the modifications of sorbose and of tagatose also differ widely from the proportions found for the configurationally related sugars, glucose and mannose. The aldoses and ketoses differ on the carbon atom involved in forming the lactol ring; that is, the structural difference is on the carbon involved in the ring-forming reaction. When viewed in this light, the differences in the equilibrium states for the aldoses and ketoses are understandable and comparable to the differences in the equilibrium states for the sugars and sugar acids.

The aldonic acids can be considered as derived from the aldoses by replacement of the hydrogen on carbon 1 by a hydroxyl. In aqueous solution, they establish equilibrium with the delta and gamma lactones.



On account of differences in the chemical properties of the acids and lactones, the composition of the equilibrium solutions for the acids can be determined more readily than the composition of the sugar solutions. In marked contrast to the sugars, the equilibrium mixtures for the aldonic acids contain larger quantities of the five-membered ring modifications (gamma lactones) and smaller quantities of the six-membered ring modifications (delta lactones). The marked difference in the equilibrium states of the aldoses, ketoses, and aldonic acids

shows that the groups attached to the carbonyl carbon greatly influence the equilibrium proportions of the open-chain and ring modifications. If the configurationally related acids are compared, it may be observed that acids which have like configurations for the α, β, γ, and δ carbons give similar equilibrium states. For example, equilibrium solutions of acids having the mannose configuration contain large proportions of the gamma lactones, while equilibrium solutions of acids having the glucose configuration contain larger proportions of the delta lactones and the free acids.

Attempts to determine the composition of sugar solutions have resulted in a number of methods for estimating the proportions of the constituents and the rates of change from one form to another, but none of these methods is entirely satisfactory. The methods may be classified roughly as (a) those which attempt to remove and study the separate constituents of the solution, and (b) those which depend on physical measurements of the solution as a whole. The removal of a constituent from the system by crystallization or chemical reaction causes an equilibrium disturbance which constitutes a limitation for all methods involving the separation of one of the constituents of the system. Measurements of physical properties, such as optical rotation, do not disturb the equilibrium, but usually the interpretation of the results is complicated, because the physical properties depend on all of the components in the solution and not on a single substance. When the components are available in the crystalline state, the information derived from freshly prepared solutions may be used to complement the results obtained with the equilibrium solutions. Information thus obtained is satisfactory for the more stable modifications in simple mixtures, but there is no really satisfactory method for determining the proportions of the labile components in complex mixtures.

2. CRYSTALLIZATION AND SOLUTION

If an equilibrium solution of glucose or another reducing sugar is concentrated and seeded with the alpha pyranose modification of the sugar in the absence of other seed, the pure alpha modification crystallizes from solution. The equilibrium disturbance caused by the separation of alpha crystals from solution causes the formation of more of the alpha isomer until finally all the sugar is converted to the alpha pyranose modification. Likewise, if the solution is seeded with the beta pyranose modification in the absence of alpha seed, the beta sugar crystallizes from solution until finally all of the sugar is converted to the beta pyranose modification. The reverse of this process, that is, the process of dissolving the sugar, has proved very useful in obtaining information concerning the equilibrium state [20, 21, 22]. If a finely powdered modification of a sugar is shaken continuously at constant temperature with a solvent in which it is only slightly soluble (so that the laws of dilute solutions apply), the solvent becomes saturated very quickly with the crystalline modification, but the sugar continues to dissolve at a slow rate. This apparent increase in solubility is caused by the conversion of the sugar into other modifications. If it is assumed that the solubility of a given modification is the same throughout the solubility experiment, the initial solubility of the crystals discloses the quantity of that modification present in the solution at any time, and the "maximum rate of solution" gives the rate of

formation of other modifications. Measurements with lactose have shown that the total sugar which will dissolve is substantially equal to the sum of the initial solubilities of the alpha and of the beta crystals. This indicates that the equilibrium solution of this sugar consists almost entirely of the two modifications. If equilibrium is established between only two modifications, alpha and beta, then, as Hudson has shown [23], the initial solubility of the alpha form (S_0), the final solubility (S_∞), and the solubility (S_t) at any time (t) measured from the beginning of the experiment may be represented by the equation,

$$1/t \ln (S_\infty - S_0)/(S_t - S_0) = k_2,$$

where k_2 is the velocity constant for the rate at which unit concentration of the beta form changes back to the alpha form. Likewise, the solubility of the beta form is given by an analogous equation,

$$1/t \ln (S_\infty - S_0')/(S_t' - S_0') = k_1,$$

in which the solubilities represent those obtained by measurements with beta crystals, and the constant (k_1) is the velocity constant for the conversion of the alpha form to the beta form. The sum of k_2 and k_1 obtained from solubility measurements with α- and β-lactose is in accord with the sum (k_1+k_2) obtained from optical-rotation measurements. The agreement of the results from the solubility and the optical rotation measurements shows that for lactose the equilibrium is satisfactorily represented by the two-component system, $\alpha \underset{k_2}{\overset{k_1}{\rightleftarrows}} \beta$. The equilibrium constant, k_1/k_2, can be calculated (1) from k_1 and k_2, as determined by the "maximum rate of solution", (2) from the initial and final solubilities by means of the relation, $k_1/k_2 = (S_\infty - S_0)/S_0$, and (3) from the optical rotations by means of the relation, $k_1/k_2 = (r\alpha - r_\infty)/(r_\infty - r_\beta)$. With lactose, glucose, and many other sugars the three methods give like values. This is evidence that for these sugars the equilibrium state is represented within experimental error by a system containing two isomers in dynamic equilibrium. Certain sugars, however, give experimental results which are not in accord with a reversible system involving only two components.

3. MUTAROTATION OF FRESHLY DISSOLVED SUGARS

(a) MUTAROTATION EQUATIONS

In 1899 Lowry suggested that the mutarotation of nitrocamphor is caused by a reversible reaction [22]. Hudson showed that the two forms of lactose give equal velocity constants for their mutarotations and, in addition, that the maximum rate of solution of the crystals is in accord with the hypothesis that the change in rotation is not caused by different reactions but by opposite parts of one balanced reaction. By applying the mass action law to the reversible reaction represented as $\alpha \underset{k_2}{\overset{k_1}{\rightleftarrows}} \beta$.

Hudson developed the following equation:

$$k_1+k_2=\frac{1}{t}\log\frac{r_0-r_\infty}{r-r_\infty}, \tag{135}$$

in which t equals the time of dissolution, r_0 the optical rotation at zero time, r the rotation at the time t, and r_∞ the final or equilibrium rotation. The mutarotation coefficient, k_1+k_2, is usually expressed in common logarithms, but if the values of k_1 and k_2 are to be applied in kinetic problems, they must be converted to a natural logarithmic base by multiplying by 2.3026. The mutarotations of glucose, lactose, mannose, and similar sugars follow the course of a first-order reaction and give satisfactory values for the mutarotation coefficients. Mutarotations which give uniform values for k_1+k_2 may be represented by an equation of the type

$$[\alpha]=A10^{-m_1t}+C, \tag{136}$$

in which $[\alpha]$ equals the specific rotation at the time t, A equals the difference between the initial and final rotation, C equals the final or equilibrium rotation, and m_1 equals the mutarotation coefficient, k_1+k_2. If the mutarotation coefficient is expressed in natural logarithms, the equation is written as an exponential function of e, as follows:

$$[\alpha]=Ae^{-kt}+C, \tag{137}$$

in which $k=(k_1+k_2)\times 2.3026$. If the logarithms of $(r-r_\infty)$ at various times are plotted against time, a linear curve is obtained provided eq 135 is applicable.

If eq 135 is not applicable, the mutarotation coefficient changes as the reaction proceeds, and the logarithms of $(r-r_\infty)$ do not fall

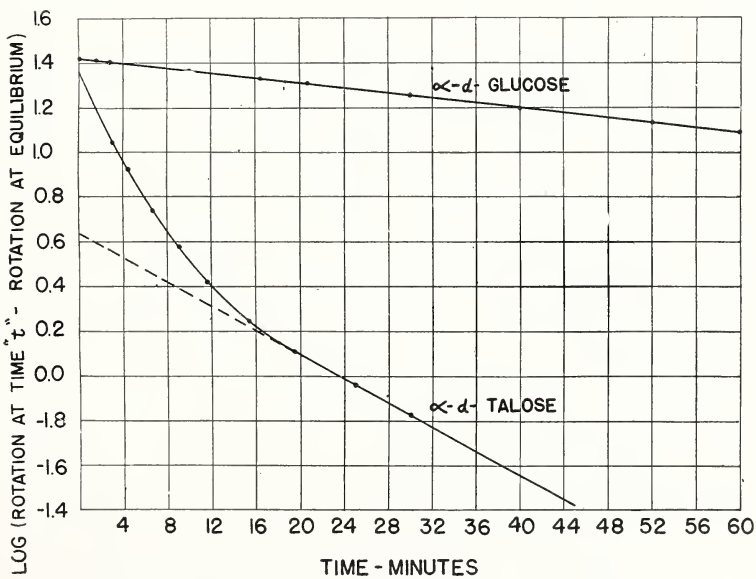


FIGURE 107.—*"Simple" and "complex" mutarotation curves.*

on a linear curve (see the curve for α-*d*-talose in fig. 107). The sugars which exhibit complex mutarotations undoubtedly establish equilibrium states which contain substantial quantities of more than two modifications of the sugar. The mutarotation reactions fall in two classes: (1) Those which are relatively slow and appear to consist in the interconversion of the alpha and beta pyranose modifications, and (2) those which are relatively rapid and appear to consist in the interconversion of the pyranose and furanose modifications.

The prevalence of systems containing more than two sugar modifications in equilibrium is shown by the work of Riiber and Minsaas [12] Riiber, [24], Sørensen [25], Smith and Lowry [13], Worley and Andrews [26], Dale [8], and Isbell [10, 11, 15, 18, 27, 28]. Riiber and Minsaas showed that the changes in "solution volume" and refractivity, which occur during the mutarotation of galactose, can be explained by assuming that equilibrium is established among three modifications. From a study of the optical rotations, Smith and Lowry also came to the conclusion that the equilibrium involves three modifications, and they developed the following equation to express the optical rotation, α, at any time, t:

$$\alpha = Ae^{-m_1' t} + Be^{-m_2' t} + C. \tag{138}$$

This equation, which is essentially the same as the one developed by Riiber and Minsaas, represents two consecutive reactions, as $x \rightleftarrows y \rightleftarrows z$. As applied to the sugar series, the equation is more or less empirical, but it appears to fit the data for the complex mutarotations as completely as eq 136 fits the simple alpha-beta interconversion. Equation 138 can be expressed to the base 10, rather than to the base e, in which case the exponents m_1 and m_2 are in common logarithms rather than in natural logarithms. In this form the equation reads

$$\alpha = A10^{-m_1 t} + B10^{-m_2 t} + C, \tag{139}$$

in which A is the change in optical rotation due to the slow or alpha-beta pyranose interconversion, B is the difference between the initial rotation and that obtained by extrapolation of the slow mutarotation to zero time, and C is the equilibrium rotation. The exponents m_1 and m_2 are functions of the velocity constants for the separate reactions which take place during the mutarotation and represent the rates at which the slow and fast changes in optical rotation occur. In order to develop equations of this type from the experimental data (see p. 156 of reference 11), the mutarotation is divided into two periods, a short period beginning at zero time, during which a rapid change occurs, and a long period beginning at the practical completion of the rapid change. By applying the formula

$$m_1 = \frac{1}{t_2 - t_1} \log \frac{r_1 - r_\infty}{r_2 - r_\infty} \tag{140}$$

to the data representing the long period (that is, the last part of the mutarotation), values of m_1 are obtained. It will be observed that m_1 is the ordinary mutarotation coefficient measured for the latter part of the mutarotation and that a mutarotation which follows the simple unimolecular course gives rise to only one exponential term. The constant, for the initial rapid change m_2 is calculated from the following equation:

$$m_2=\frac{1}{t'_2-t'_1}\log\frac{d_1}{d_2}, \tag{141}$$

in which d_1 and d_2 represent the differences between the observed rotations and those obtained by extrapolation of the long period back to the corresponding times. The extrapolation is accomplished mathematically by substitution in eq. 140

TABLE 59.—*Mutarotation of α-d-galactose* [*11*]
5.0 g per 100 ml at 20.0° C read in a 4-dm tube.
$°S=37.51\times10^{-.00803\,t}+3.25\times10^{-.079\,t}+46.34.$
$[\alpha]_D^{20}=°S\times1.7307.$

Time	Saccharimeter reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$
1	2	3	4	5	6
Minutes	°*S*			°*S*	
1.9	+84.85	----------	----------	2.30	----------
3.0	+83.67	12.3	----------	1.84	88.1
4.4	+82.44	11.3	----------	1.52	72.0
6.6	+80.54	11.0	----------	1.00	77.0
8.6	+79.03	10.6	----------	0.69	78.0
10.2	+77.95	10.3	----------	.55	74.9
12.0	+76.73	10.2	----------	.34	83.9
14.8	+75.09	9.8	----------	.22	79.0
29.7	+68.00	9.0	----------	----------	----------
45.0	+62.66	8.7	8.04	----------	----------
59.8	+58.75	8.5	8.04	----------	----------
80.0	+54.92	8.4	8.00	----------	----------
100.7	+52.18	8.3	8.02	----------	----------
119.5	+50.47	8.2	8.01	----------	----------
149.9	+48.66	8.2	8.07	----------	----------
∞	+46.34	----------	----------	----------	----------
Average	----------	----------	8.03	----------	79.0

The following example is based on the data for the mutarotation of α-*d*-galactose, table 59, and is given to clarify this description. Column 2 gives the observed rotations at the indicated times. The calculation of m_1 is begun at 29.7 minutes, as calculations started at earlier times give a drift in the constant. The values of m_1 given in column 4 are obtained by application of eq 140, using $r_1=+68.00$, $t_1=29.7$, and for r_2, readings taken at later times. The slow reaction is carried back to times earlier than 29.7 minutes by substituting the average value of m_1, (8.03×10^{-3}), in eq 140, and solving for r_1 at each of the times, t_1, earlier than 29.7 minutes (including zero time), using $r_2=+68.00$, $r_\infty=+46.34$, and $t_2=29.7$. (The equilibrium rotation, r_∞, subtracted from the calculated value at zero time, gives A in eq 139.) These values, subtracted from the observed rotations at the corresponding time, give the differences shown in column 5 of the table. The constant, m_2, for the rapid change is then obtained by substituting the differences in eq 141, using $d_1=2.30$, $t'_1=1.9$, and for d_2 the values recorded at the later times, t'_2. By placing the average value of m_2 (79.0×10^{-3}) in eq 141, and using $d_2=2.30$ and $t'_2=1.9$, the value of d_1 at zero time, t'_1, may be obtained by solving the equation. The value so obtained (3.25) is that to be used for B in eq 139. The equilibrium rotation (46.34) is C; A (37.51) is the difference between

the equilibrium rotation (46.34) and the calculated value of r_1 at zero time (83.85), which has already been obtained by application of eq 140. The substitution of these values in eq 139 gives the equation.[41]

$$^{\circ}S=37.51\times10^{-.00803t}+3.25\times10^{-.079t}+46.34. \qquad (142)$$

If it is desired to use the natural logarithmic base, eq 142 is changed only by replacement of the base 10 by the base e, and by multiplying each of the exponents by 2.3026. The equation, which expresses the optical rotations as observed, is converted to a specific rotation by multiplying by the ratio of the equilibrium specific rotation to the observed equilibrium rotation. For example, in the mutarotation represented by eq 142, the equilibrium specific rotation of galactose was found from a separate experiment to be 80.2. The ratio of the equilibrium specific rotation to the observed equilibrium rotation is 80.2/46.34, or 1.7307. Multiplying eq 142 by this factor gives the mutarotation in terms of specific rotation.

A summary of some mutarotation measurements, which have been conducted at the National Bureau of Standards during recent years, is given in table 149, p. 762 of this publication. The measurements reported therein were conducted as described in the following paragraph.

(b) MEASUREMENT OF MUTAROTATION

Mutarotation measurements are conveniently made in the following manner: The carefully purified sugar is powdered in an agate mortar and passed through a fine sieve. The weighed sample (about 2 g) is placed in a dry 100-ml glass-stoppered flask and about 50 ml of distilled water (preferably of known pH, or buffered with 0.001 N potassium acid phthalate,)[42] at the correct temperature is added with agitation. The water can be added conveniently from a fast-draining pipette. Time, beginning with the addition of the water, is measured with a stop watch. After the sugar is dissolved, the solution is transferred to a water-jacketed polariscope tube and maintained at the desired temperature while optical rotation measurements are made. The work is preferably conducted in a room held at the temperature selected for the measurement; in any case, the water which circulates in the jacket of the polariscope tube should be held at constant temperature by a suitable thermostat. The optical rotations are measured directly after the solution of the sugar, and at such times thereafter as required to disclose the changes that occur. It is convenient for one person to make polariscope readings while another notes the times and records the results. It is usually advisable to make the observations in groups of 5 or 10 readings which (unless mutarotation is taking place rapidly) can be averaged for use in calculating the velocity constants. The method used for calculating the equations to represent the mutarotations and the mutarotation coefficients is given on page 444.

The equilibrium specific rotation of the sugar is determined with a separate sample of the sugar. It is necessary to use the same concentration and temperature as those employed in the mutarotation measurements.

[41] The optical rotation was read in sugar degrees.
[42] 0.2041 g of potassium acid phthalate (NBS Standard Sample 84) dissolved in 1 liter of water.

(c) VELOCITY AND EQUILIBRIUM CONSTANTS FOR THE MUTAROTATION REACTIONS

As already mentioned, the mutarotations of certain sugars consist of two or more reactions which involve three or more substances in dynamic equilibrium. The calculation of the separate velocity and equilibrium constants for all the mutarotation reactions is scarcely feasible at present because the number and character of the reactions are not known. By postulating that the mutarotation involves only two isomers, the separate velocity and equilibrium constants may be calculated from k_1+k_2 (eq 135, p. 443), and the equilibrium constant k_1/k_2, which is obtained from the optical rotations by the equation

$$\frac{k_1}{k_2}=\frac{r_\alpha-r_\infty}{r_\infty-r_\beta}. \tag{143}$$

Some values of k_1 and k_2 thus calculated are given in table 60.

TABLE 60.—*Equilibrium constants calculated from optical-rotation measurements, assuming that only two isomers are present in dynamic equilibrium*

Sugar	Temperature	Mutarotation coefficient [1]	Optical rotation			Velocity constants [2]		
		k_1+k_2	$[\alpha]_D$, α-isomer	$[\alpha]_D$, β-isomer	$[\alpha]_D$, equilibrium mixture [1]	k_1	k_2	$\frac{k_1}{k_2}$
	° C							
d-Lyxose	20	0.0580	+5.6	−72.6	−13.8	0.0144	0.0436	0.330
	0.2	.00842	+4.7	−70.8	−13.4	.00202	.00640	.315
d-Glucose	20	.00629	+112.2	+18.7	+52.7	.00400	.00229	1.750
	0.2	.000740	+111.5	+18.4	+52.1	.000472	.000268	1.763
d-Mannose	20	.0176	+29.3	−17.0	+14.2	.0057	.0119	0.484
	0.3	.00215	+28.8	−16.7	+14.6	.00067	.00148	.454
d-Lactose	20	.00469	+89.5	+34.9	+55.4	.00293	.00176	1.663
	0.2	.000534	+90.9	+36.3	+56.4	.000337	.000197	1.716

[1] Average of values obtained from the alpha and beta isomers.
[2] Expressed in minutes and in logarithms to the base 10.

(d) EFFECT OF TEMPERATURE ON THE MUTAROTATION RATE

In accordance with the general behavior of chemical reactions, the velocity for the mutarotation of a sugar is accelerated by a rise in temperature. Between 25° and 35° C the rates increase from one and one-half to three times, depending upon the sugar and upon the character of the mutarotation reaction. The normal alpha-beta pyranose interconversions have higher temperature coefficients than the rapid mutarotation reactions (pyranose-furanose interconversions).

The effect of temperature on the rate of mutarotation is represented most satisfactorily by means of the integrated Arrhenius equation,

$$\ln\frac{k'}{k''}=\frac{Q}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right), \tag{144}$$

in which k' and k'' are velocity constants at the absolute temperatures, T_1 and T_2; R is the gas content; and Q is the heat of activation. In 1904 Hudson determined the effect of temperature on the velocity

constants for the conversion of alpha to beta lactose and for the conversion of beta to alpha lactose. Subsequently, Lowry [4, p. 102] calculated, from Hudson's data, the following heats of activation:

	0° to 15° C.	15° to 25° C.	Mean
	Cal.	*Cal.*	*Cal.*
Heat of activation $\alpha \longrightarrow \beta$ calculated from k_1	17, 730	18, 800	18, 300
Heat of activation $\beta \longrightarrow \alpha$ calculated from k_2	17, 100	18, 000	17, 500

Application of the integrated Arrhenius equation to the data in table 60 gives the following heats of activation:

$$\alpha\text{-Glucose} \xrightarrow{k_1} \beta\text{-Glucose} = 17{,}170 \text{ cal.}$$
$$\beta\text{-Glucose} \xrightarrow{k_2} \alpha\text{-Glucose} = 17{,}240 \text{ cal.}$$
$$\alpha\text{-Lactose} \xrightarrow{k_1} \beta\text{-Lactose} = 17{,}380 \text{ cal.}$$
$$\beta\text{-Lactose} \xrightarrow{k_2} \alpha\text{-Lactose} = 17{,}600 \text{ cal.}$$

$$\alpha\text{-Mannose} \xrightarrow{k_1} \beta\text{-Mannose} = 17{,}300 \text{ cal.}$$
$$\beta\text{-Mannose} \xrightarrow{k_2} \alpha\text{-Mannose} = 16{,}840 \text{ cal.}$$
$$\alpha\text{-Lyxose} \xrightarrow{k_1} \beta\text{-Lyxose} = 15{,}780 \text{ cal.}$$
$$\beta\text{-Lyxose} \xrightarrow{k_2} \alpha\text{-Lyxose} = 15{,}420 \text{ cal.}$$

It may be observed that the heats of activation for the alpha-pyranose isomers do not differ widely from the heats of activation for the beta-pyranose isomers. If the heat of activation for the alpha isomer equals that for the beta isomer, the value of Q obtained by application of the Arrhenius equation to the mutarotation coefficient (k_1+k_2) likewise is equal to the same heat of activation. If the heats of activation of the alpha and beta isomers as calculated from k_1 and k_2 are not equal, the value of Q obtained from the mutarotation coefficient (k_1+k_2) is not a true heat of activation. Nevertheless, it is useful for comparing mutarotation measurements at different temperatures and for differentiating between mutarotation reactions of different types. Isbell and Pigman [11] found that the values of Q obtained from the mutarotation coefficients for the alpha-beta pyranose interconversions are larger than the values obtained from the mutarotation coefficients for the pyranose-furanose interconversions.

(e) EFFECT OF TEMPERATURE ON THE EQUILIBRIUM STATE

The effect of temperature on the equilibrium state can be ascertained most readily by observing the mutarotation which follows a change in temperature. When a sugar solution is cooled rapidly, a nearly instantaneous change in optical rotation takes place. This is followed by a mutarotation, the direction and rate of which furnish

quantitative information concerning the shift in equilibrium. Mutarotations of this character are called thermal mutarotations. In 1909 Hudson [29] observed that when a solution of glucose, galactose, xylose, lactose, or maltose is cooled, a very small mutarotation takes place, from which he concluded that, at the higher temperature, the equilibrium solution contains more of the alpha sugar. The investigations of Isbell have shown that the equilibrium state between the alpha and beta pyranose modifications changes only slightly with changes in temperature, whereas the equilibrium state between the pyranose and furanose modifications changes considerably with temperature. Usually in the mutarotations of the freshly dissolved sugars, the changes due to the alpha-beta pyranose interconversions are large in comparison with those due to pyranose-furanose interconversions. In the thermal mutarotations, however, the changes due to the alpha-beta pyranose interconversions are small in comparison with those due to the pyranose-furanose interconversions. Consequently, the thermal mutarotations are useful for estimating the velocity constants for the pyranose-furanose interconversions. Some typical thermal mutarotations are given in table 61.

The relatively large temperature effects for the pyranose-furanose equilibrium indicate that the heats of reaction are considerable; correspondingly small changes in the alpha-beta pyranose equilibrium indicate that the heats of reaction for the alpha-beta interconversions are small.

The heat of reaction (ΔH) can be calculated from the equilibrium constants, but unfortunately in most cases these are not known. Application of the Van't Hoff equation

$$\ln \frac{K_1}{K_2} = \frac{-\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

to the equilibrium constants given in table 60 gives, for the heat of reaction in calories, values of +374, −59, +517, and −252 for the mutarotations of lyxose, glucose, mannose, and lactose, respectively. By direct measurement Brown and Pickering [30] found a thermal change of −835 calories per gram molecule for the mutarotation of levulose and smaller values for the mutarotations of dextrose, lactose, and maltose. Riiber and Minsaas [12] found that the rapid mutarotation reaction of *α-d*-galactose is accompanied by the absorption of heat, whereas the slow alpha-beta interconversion is accompanied by the liberation of heat.

TABLE 61.—*Thermal mutarotation for sugars exhibiting complex mutarotation.*

Thermal mutarotation of a 10-percent aqueous solution of *d*-galactose after cooling it from 25° to 0.3° C. $°S = 1.10 \times 10^{-.00107t} - 3.49 \times 10^{-.0132t} + 97.87$

Time [1]	Saccharimeter reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$
Minutes	°S		°S	
5.74	+96.02	.....	−2.93	.....
6.95	+96.13	.....	−2.82	13.8
10.00	+96.49	.....	−2.45	18.2
15.13	+96.74	.....	−2.19	13.5
20.09	+97.04	.....	−1.88	13.4
26.15	+97.32	.....	−1.58	13.1
30.20	+97.46	.....	−1.43	12.7
40.27	+97.76	.....	−1.10	12.3
50.11	+98.02	.....	−0.82	12.5
60.96	+98.23	.....	−.59	12.6
75.23	+98.41	.....	−.37	12.9
89.97	+98.48	.....	−.27	12.3
126.54	+98.53	.....	−.14	10.9
139.88	+98.60	.....	−.05	13.2
160.18	+98.61	.....	.....	.....
244.19	+98.45	1.26	.....	.....
306.1	+98.39	1.05	.....	.....
365.2	+98.30	1.15	.....	.....
502.1	+98.24	0.88	.....	.....
738.7	+98.06	1.02	.....	.....
∞	+97.87	.....	.....	.....
Average	.....	1.07	.....	13.2

Thermal mutarotation of an 8-percent aqueous solution of *l*-arabinose after cooling it from 25.2° to 0.2° C. $°S = 1.52 \times 10^{-.00364t} - 4.56 \times 10^{-.0271t} + 101.71$

4.57	+99.74	.....	−3.43	.....
5.94	+100.01	.....	−3.15	27.0
8.29	+100.38	.....	−2.75	25.8
10.64	+100.75	.....	−2.35	27.1
15.16	+101.30	.....	−1.75	27.6
20.21	+101.71	.....	−1.28	27.4
25.58	+102.01	.....	−.93	27.0
30.06	+102.20	.....	−.69	27.3
40.10	+102.45	.....	−.35	27.9
51.15	+102.55	.....	−.12	(31.3)
75.14	+102.52	.....	.....	.....
90.19	+102.41	4.21	.....	.....
121.06	+102.26	3.66	.....	.....
154.66	+102.11	3.85	.....	.....
184.1	+102.06	3.34	.....	.....
214.6	+101.98	3.42	.....	.....
277.9	+101.87	3.47	.....	.....
330.6	+101.81	3.56	.....	.....
389.9	+101.77	3.59	.....	.....
∞	+101.71	.....	.....	.....
Average	.....	3.64	.....	27.1

[1] Measured from the beginning of the cooling process.

(f) EFFECT OF ACIDS AND BASES ON THE MUTAROTATION RATES

The acceleration of the mutarotation rates of the sugars by acids and bases has been the subject of many investigations. The early workers attributed the catalytic effect of acids and bases to the hydrogen and hydroxyl ions, but subsequent work has revealed that catalysis is not the exclusive property of the hydrogen and hydroxyl ions. Experiments by Lowry and coworkers, [4, p. 111,] by Brönsted and Guggenheim [31], and others have disclosed the catalytic activity of molecules of undissociated acids, of anions of weak acids, and of cations of weak bases. In general, amphoteric solvents are complete catalysts for the mutarotation, while hydrocarbons, chloroform, and carbon tetrachloride do not promote mutarotation.

It may be observed from the curve given in figure 108 that the velocity for the mutarotation of glucose in aqueous solutions does not change appreciably in the range from pH 2.5 to 6.5. However, in more

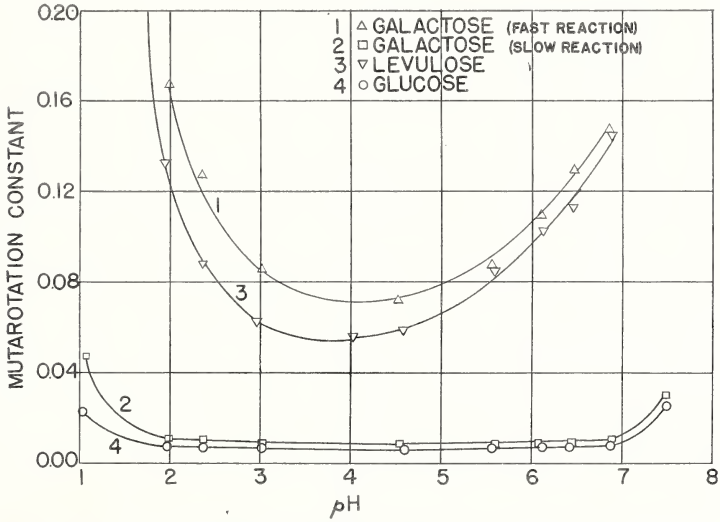


FIGURE 108—*Variation of the mutarotation constants with* pH [*10*].

strongly alkaline or acid solutions, the velocity rises rapidly with increasing concentrations of the hydrogen and hydroxyl ions. If carefully purified distilled water, free from carbon dioxide, is employed in mutarotation measurements, the velocity constants are substantially higher than those obtained in slightly acid solutions. Fortunately the region of minimum velocity falls in the pH range of distilled water containing carbon dioxide, such as the water ordinarily used for mutarotation measurements. Minute quantities of bases suffice to cause large alterations in the rate, and therefore it is difficult to obtain satisfactory velocity constants except in the presence of an acid-base buffer. Mutarotation measurements made with unbuffered solutions in nickel, brass, or copper tubes give substantially higher velocity constants than those made in glass tubes [32]. The higher constants appear to be due to an alteration in the acidity caused by the metallic oxide from the tubes which dissolves in the sugar solution.

Precautions are necessary in making mutarotation measurements to avoid accidental catalysis. In order that results from different sources be placed on a comparable basis, the use of 0.001 N potassium acid phthalate is recommended as a solvent for mutarotation measurements. According to Hudson, the catalytic activity of water in the mutarotation of glucose may be represented by the equation

$$k=0.0096+0.258[H^+]+9750\ [OH^-].$$

The equation shows that the alterations caused by the hydrogen and hydroxyl ions are proportional to their concentration but that there is a residual catalytic activity which is now considered to be due to undissociated water molecules.

In the mutarotation of glucose at pH 4.7, the contribution of the hydroxyl ion to the catalysis is about 40,000 times that of the hydrogen ion, and the residual catalytic effect of the water is nearly 500 times that of the combined catalytic effect of the hydrogen and hydroxyl ions.

Lowry and Faulkner [33] showed that pure pyridine and pure cresol do not promote mutarotation; however, a mixture of 1 part of pyridine with 2 parts of cresol does accelerate the rate for the mutarotation of tetramethyl glucose to 20 times that obtained in water solution. Lowry explained this seemingly anomalous behavior by assuming that for the mutarotation to take place the solvent must possess acid and basic properties simultaneously. Pyridine and cresol, or pyridine and water, or water alone, can act both as an acid and as a base, but pyridine alone can act only as a base and cresol alone can act only as an acid. In this connection the acid and basic functions are used in the Brönsted sense, that is, the ability to give or to accept protons. The molecules of an undissociated acid can give, and the anions of a weak acid can accept, a proton, as follows:

$$CH_3COOH \longrightarrow \text{gives } H^+ + CH_3COO^-$$

$$CH_3COO^- \text{ accepts } H^+ \longrightarrow CH_3COOH$$

The ammonium cation can give a proton, and ammonia can accept a proton as follows:

$$NH_4^+ \text{ gives } H^+\text{, leaving } NH_3$$

$$NH_3 \text{ accepts } H^+\text{, giving } NH_4^+$$

Undissociated water accepts a proton and forms the H_3O^+ ion or gives a proton and forms the hydroxyl ion. The anions of highly ionized strong acids and metallic cations do not give or accept protons and hence do not exhibit catalytic activity. In harmony with this concept, calcium chloride, sodium sulfate, and other metallic salts of strong acids do not accelerate the mutarotation reaction, while salts of weak acids, like sodium acetate, have marked catalytic action. Isbell and Pigman [10] have shown that the mutarotation of levulose and the rapid mutarotation of galactose are extremely sensitive to the catalytic action of acids and bases. The extreme sensitivity of the pyranose-furanose interconversions to acid and basic catalysts furnishes a convenient means for distinguishing them from the alpha-beta pyranose interconversions.

(g) EFFECT OF THE SOLVENT AND OTHER SUBSTANCES ON THE EQUILIBRIUM STATE

The optical rotations of the reducing sugars in different solvents vary widely. The variation results, in part from the fact that a given constituent will have different optical rotations in different solvents, and in part from the displacement of the equilibrium between the various sugar modifications. The effect of a change in the solvent on the equilibrium state can be ascertained most readily by observing the mutarotation which follows a change of solvent. For example when a concentrated aqueous solution of galactose is diluted with several volumes of alcohol, a nearly instantaneous change in optical rotation takes place. This is due to the difference in the optical rotations of the constituents because of the change in solvent. The initial change in rotation due to the new solvent is followed by a complex mutarotation reaction which apparently consists of the rapid

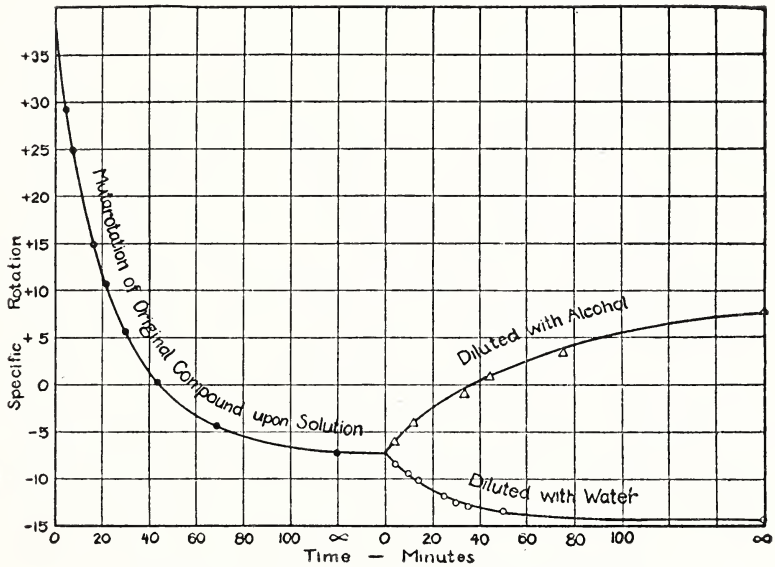


FIGURE 109.—*Mutarotation of d-gulose* $CaCl_2H_2O$.

and slow mutarotation reactions previously discussed. This complex mutarotation shows that in some manner the equilibrium between the various constituents is altered by a change in solvent. The effect of solvents on the equilibrium state has not been investigated very thoroughly. Apparently in some cases the solvent combines with the sugar, and may facilitate the separation of different modifications of the sugar. For example, *d*-glucose crystallizes from pyridine solutions in the form of a pyridine compound which contains the beta pyranose modification; while from water solutions at ordinary temperatures *d*-glucose crystallizes in the form of a hydrate which contains the alphapyranose modification. The existence of numerous solvated sugars and sugar derivatives shows that the solvent is not merely an inert medium in which the sugar is dissolved. Isbell [34] has shown that the position of the equilibrium between the various modifications

of *d*-gulose in solution can be altered by the addition of calcium chloride, or by changing the concentration of *d*-gulose calcium chloride. The mutarotation which follows a change in the concentration of *d*-gulose calcium chloride indicates that in some manner the sugar equilibrium is displaced by the change in concentration. The addition of a salt to the system complicates the equilibrium conditions by forming molecular compounds with the various isomeric forms of the sugar, some of which compounds have been isolated. In dilute solution the compounds are largely dissociated into the sugar and calcium chloride. As shown by the curves given in figure 109, dilution of a concentrated solution of *d*-gulose $CaCl_2.H_2O$ with water results in the formation of the more levorotatory modification of *d*-gulose, while dilution with alcohol results in the formation of the more dextrorotatory modification. Obviously the equilibrium existing in an alcoholic solution of *d*-gulose $CaCl_2.H_2O$ is different from the equilibrium existing in an aqueous solution. Similarly, the equilibrium of *d*-α-glucoheptose is shifted by calcium chloride in a manner comparable to the shift observed for *d*-gulose [35].

Another interesting example of the influence of calcium chloride on the equilibrium state is the formation of a calcium chloride compound of the furanose modification of *d*-mannose [8, 9]. A pure aqueous solution of *d*-mannose does not appear to contain an appreciable quantity of the furanose modification, but when calcium chloride is added to the mannose solution and the solution evaporated, *d*-mannofuranose calcium chloride crystallizes.

4. CHEMICAL METHODS FOR STUDYING THE EQUILIBRIUM STATE

When a sugar is treated with methyl alcohol in the presence of hydrochloric acid, the alpha and beta methyl pyranosides and the alpha and beta methyl furanosides are formed. The furanosides are formed much more rapidly than the pyranosides, so that with short treatment at low temperatures, the furanosides predominate, whereas with longer treatment at higher temperatures, the pyranosides predominate. Obviously, on account of the equilibrium displacement, the formation of either the furanosides or the pyranosides does not give information concerning the equilibrium existing in the original solution. But under favorable conditions, by consideration of the mechanism of the reaction and of the rates at which the various modifications change one into another, one can interpret a chemical reaction in terms of the equilibrium state. The most extensive investigation of this character has been made on the oxidation of the sugars with bromine [36, 37, 38]. In slightly acid solution the pyranose sugars are oxidized rapidly to delta lactones (as shown by the results given in [9, 37]), whereas the furanose sugars are oxidized to gamma lactones. Since the oxidation is rapid in comparison with the rate at which one modification of the sugar changes to another, the identification of the oxidation products indicates which substances are present in the equilibrium solution. The alpha and beta sugars differ widely in their rates of reaction. The oxidation of the sugar in the equilibrium solution proceeds rapidly until the easily oxidizable beta modification is used up, and more slowly as the difficultly oxidizable alpha modification continues to be oxidized. By comparing the rates of oxidation of the sugar in the equilibrium solution with the rates for the alpha and

beta modifications as determined separately, it is possible to calculate the proportions of each modification in the equilibrium solution. Table 62 gives results of work reported by Isbell [27, 37] and by Isbell and Pigman [11].

TABLE 62.—*Oxidation of sugar solutions at 0° C with bromine water in the presence of barium carbonate* [a]

Sugar	Composition of equilibrium solution				Rate of oxidation with bromine water at 0° C			
	Estimated from oxidation measurement		Calculated from optical rotation, assuming only two constituents		Obtained with equilibrium solutions at 0.3° C		Obtained with crystalline sugars	
	Less reactive sugar	More reactive sugar	Alpha sugar	Beta sugar	$k_A \times 10^3$	$k_B \times 10^3$	$k\alpha \times 10^3$	$k\beta \times 10^3$
	Percent	*Percent*	*Percent*	*Percent*				
l-Arabinose	32.4	67.6	26.5	73.5	84.2	1,608	95.3	1,658
d-Xylose	32.1	67.9	[b] 34.8	[b] 65.2	80.3	1,673	89.9	--------
d-Lyxose	79.7	20.3	76.0	24.0	189	717	156	449
d-Ribose	89.3	10.7	--------	--------	180	1,010	196	--------
l-Ribose	89.0	11.0	--------	--------	170	1,456	195	--------
l-Rhamnose	69.0	31.0	[b] 73.1	[b] 26.9	83.4	770	89.7	--------
d-Glucose	37.4	62.6	36.2	63.8	27.5	1,362	32.4	1,255
d-Mannose	68.9	31.1	68.8	31.2	45.2	860	51.1	781
d-Galactose	31.4	68.6	29.6	70.4	37.9	1,720	42.3	1,590
d-Talose	55.9	44.1	--------	--------	84.8	844	78.5	--------
$(d\text{-Gulose})_2CaCl_2.H_2O$	18.5	81.5	--------	--------	52.6	418	54.8	328
d-α-Mannoheptose hydrate	32.8	67.2	--------	--------	49.7	1,556	40.4	1,843
d-β-Guloheptose	37.0	63.0	--------	--------	39.1	1,779	34.2	--------
d-β-Galaheptose	37.2	62.8	--------	--------	25.5	1,987	--------	1,696
d-α-Galaheptose hydrate	79.4	20.6	--------	--------	65.0	1,797	72.1	--------
d-α-Glucoheptose	11.8	88.2	--------	--------	44.2	458	--------	393
d-β-Glucoheptose	21.9	78.1	--------	--------	30.2	382	--------	355
Lactose	37.5	62.5	36.8	63.2	20.9	1,475	29.3	952
Maltose	37.7	62.3	[b] 36.0	[b] 64.0	23.7	1,388	--------	1,528

[a] The experimental details for the oxidation measurements are given on p. 173 of reference [11]. Rates of oxidation were determined in aqueous solutions containing 0.05 mole of sugar per liter, and approximately 0.08 mole of free bromine per liter, and buffered with barium carbonate and carbon dioxide.
[b] Percentage calculated from Hudson's optical rotations derived from measurements of the initial and final solubilities at 20° C.

The reaction of the sugars with hydrogen cyanide has been used for estimating the concentration of the open-chain modifications. It is assumed that the open-chain modifications of the sugars combine readily with hydrogen cyanide, whereas the ring modifications do not. Lippich [39] has shown that each sugar in the equilibrium state has an initial power for combining with hydrogen cyanide, which he considers a measure of the amount of the open-chain modification present in the equilibrium state.

The reaction of the sugars with acetic anhydride in pyridine solution appears to give some information concerning the modifications present. Schlubach and Prochownick [40] found, for example, that the proportions of the pyrano- and furano-acetates of galactose, formed by acetylation of galactose dissolved in dry pyridine vary with temperature. The reaction of the sugars with acetone in the presence of copper sulfate also has been used to show the presence of furanose modifications [41]. In conclusion, further investigation of the reaction rates and the quantitative determination of the products is needed to give additional information concerning the equilibrium state.

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XXX. METHODS FOR THE PREPARATION OF CERTAIN SUGARS

The methods reported here are those ordinarily used in the laboratories of the National Bureau of Standards for the preparation of the various sugars. No attempt has been made to give a complete bibliography or to record the contributions of the various workers in the field. Some of the methods are essentially as given in the reference cited, while others have been improved in various ways.

1. *d*-ALLOSE

Method.[1]—[1, 2, 3][43]. Fifty grams of purified *d*-allonic lactone[2] and 500 ml of distilled water are placed in a 1.5-liter wide-mouthed

[43] In chapters XXX and XXXI the superscript numbers refer to the numbered notes, and the numbers in brackets refer to literature reference numbers at the end of each section.

flask or beaker. The solution is stirred vigorously and cooled in an ice-and-salt bath so that a little ice forms inside the beaker (to be sure that the solution is actually at about 0° *C*). About 4 ml of dilute (10-percent) sulfuric acid is added, and then 2.5-percent sodium amalgam in 250-g portions, while dilute sulfuric acid is continuously dropped from a burette at such rate that the solution remains just barely acid to congo-red test paper.[3] After the addition of 3 or 4 portions of amalgam during the course of approximately 1 hour, the sugar content reaches a maximum. The solution is poured off from the mercury and treated with enough sodium carbonate so that after standing about ½ hour (cold) the reaction mixture is still slightly alkaline.[4] Dilute sulfuric acid is added until the solution is slightly acid to litmus; it is then evaporated in vacuo to a small volume. Alcohol is added until further addition causes no further precipitate, the solution is filtered, and the alcoholic filtrate evaporated to a thick sirup. Upon extraction of the sirup with hot absolute alcohol, the allose dissolves, leaving sodium allonate as a sticky gum. Evaporation of this alcoholic extract yields crystalline allose.

The crude product may be purified by dissolving it in a little warm water, adding 3 volumes of warm methyl alcohol, and filtering through a little decolorizing carbon. The filtrate is allowed to cool and is seeded with crystalline allose. After standing for several hours, the crystalline product is separated.

NOTES

[1] The same procedure may be used for the preparation of altrose and other sugars.

[2] The preparation of allonic lactone from ribose is described on page 527.

[3] The solution should be kept cold and the acidity should be carefully watched.

[4] The purpose of the sodium carbonate treatment is to convert all unreduced lactone to the sodium salt in order to facilitate its removal by alcohol.

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2. *l*-ARABINOSE

Method.[1]—[1] Three kilograms of mesquite gum [2] is dissolved in 11 liters of water.[3] Two liters of a solution containing 370 ml of concentrated sulfuric acid is added, and the solution is kept for 7 hours at a temperature of 80° to 90° C. The hot solution is neutralized with about 700 g of calcium carbonate,[4] and the insoluble material is removed by filtration. To the filtrate is added 1 kg of decolorizing carbon.[5] After several hours the solution is filtered and the filtrate evaporated in vacuo to a volume of 4 liters. Twelve liters of hot ethyl alcohol is now added and the two phases are thoroughly mixed.[6] The gummy material is allowed to settle out for several hours while the liquid cools. The supernatant liquid is separated by decantation. The gums are given a second and third extraction, each time with 6 liters of warm methyl alcohol. The alcoholic extracts are combined and concentrated in vacuo to a thin sirup which is allowed to crystallize. About 900 g of crude arabinose is obtained in the first crop and 250 g of additional material may be separated by concentrating the

mother liquors, removing the gummy impurities by precipitation with hot ethyl alcohol and evaporating the alcoholic extract.[7]

Recrystallization.—Crude arabinose which contains gums may be purified in the following manner: 300 g of the sugar is dissolved by heating with 100 ml of water; the solution is mixed with 750 ml of hot ethyl alcohol and 15 g of a decolorizing carbon. The hot solution is filtered, and the carbon residue is washed with 150 ml of hot ethyl alcohol. The hot filtrate is allowed to cool, and accidental seeding with crystalline arabinose is avoided. As the solution cools it separates into two phases, the lower more sirupy layer of which contains most of the impurities. After the solution reaches room temperature and the sirupy phase has settled, the alcoholic layer is decanted. The residue is extracted as before with 300 ml of hot methyl alcohol, followed by 300 ml of hot ethyl alcohol. The combined alcoholic extract is evaporated in vacuo to a volume of approximately 600 ml. Sometime before this volume is reached, crystallization takes place in the distillation flask. When the evaporation has reached the desired stage, the sirup is seeded with crystalline arabinose, placed in the refrigerator, and allowed to stand until a satisfactory crystal growth is obtained. The first crystals are usually about 60 percent of the arabinose content. By concentrating the mother liquors, additional crystalline sugar is obtained.

Relatively pure arabinose can also be recrystallized in the following manner: 300 g of arabinose is dissolved with 180 ml of water. The hot solution is mixed with 200 ml of hot methyl alcohol, and after the addition of 50 g of a decolorizing carbon the mixture is filtered rapidly while hot. The filtrate is diluted with 400 ml of methyl alcohol and 300 ml of ethyl alcohol, cooled to room temperature, seeded, and set aside to crystallize. After several days the resulting crystals are collected on a filter and washed with methyl alcohol. The yield is about 150 g. The sugar in the mother liquors is reclaimed by evaporating the liquors to a sirup ($n_D^{20}=1.465$), which, after mixing with about 5 volumes of methyl alcohol, yields additional crystalline sugar.

In 4-percent aqueous solution, β-*l*-arabinose gives $[\alpha]_D^{20}=+190.6°$ initially, which changes in the course of several hours to $+104.5°$.

NOTES

[1] The method is that of Anderson and Sands [1] as modified by Isbell (heretofore unpublished work).

[2] Mesquite gum is obtained from a plant (*Prosopis juliflora* and related species) widely distributed through the southwest. It may be purchased from the Martin Drug Co., Tucson, Ariz. Cherry gum may also be used with essentially the same procedure.

[3] The gum requires about 24 hours to dissolve. Before starting the hydrolysis, it is well to filter the solution through cheese cloth in order to remove bark and other foreign matter.

[4] This must be done slowly with small portions of calcium carbonate. Foaming may be reduced by the addition of a commercial antifoam agent or capryl alcohol.

[5] The exceptionally large quantity of decolorizing carbon is added to reduce foaming, which can be further reduced by the use of an antifoam agent such as capryl alcohol.

[6] A mechanical stirrer is of considerable help in this procedure.

[7] *l*-Arabinose has been prepared from a number of other sources: Cherry gum [2], wheat and rye bran [3, 4], peach gum [5], Australian black wattle gun [6], and beet pulp [7]. Harding [8] gives a review of the sources.

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3. CELLOBIOSE (4-(β-*d*-GLUCOPYRANOSIDO)-*d*-GLUCOSE)

Method.—The octaacetyl cellobiose is prepared by the action of acetic anhydride and sulfuric acid on cotton or filter paper according to the method of Klein [1].[1] Fifty grams of pure cotton is put in a precipitating jar (about 12 cm in diameter and 25 cm high), which is cooled in an ice-and-salt bath. Acetic anhydride, 140 ml, is added and the jar covered with a watch glass. Sixty milliliters of acetic anhydride is cooled in an ice-and-salt bath and 28 ml. of sulfuric acid slowly added. When this solution has cooled, it is poured onto the cold mixture of cotton and acetic anhydride and the whole mixture worked to a homogeneous mass by stirring with a glass rod. The cotton gradually disintegrates. The mass is transferred to a 2-liter Erlenmeyer flask and after vigorous shaking and occasional heating on the steam bath, a reddish solution is obtained.[2] Several such batches combined are allowed to stand at room temperature for 2 or 3 days while crystallization takes place. The crystalline mass is not poured into water, as described by Klein, but filtered on a large-size Büchner filter having small holes, and fitted with a double layer of ordinary filter paper. It is filtered dry and washed with ether. The product is now stirred in a dish with 95-percent alcohol, again filtered by suction, and finally recrystallized from 95-percent alcohol. The yield may reach 40 to 50 percent of the theoretical. In a 2.5-percent concentration in chloroform the specific rotation of the pure substance is $[\alpha]_D^{20}=+41.5°$, and the melting point is 229.5° C.

The cellobiose octaacetate is deacetylated by dissolving it in dry methyl alcohol and adding 1 ml of 0.5 *N* barium methylate [3] solution for each gram of sugar. After standing overnight in the refrigerator, the barium is removed by precipitation with an equivalent quantity of sulfuric acid and the barium-free solution is concentrated in vacuo to a thin sirup which on standing yields crystalline cellobiose.

Anhydrous β-cellobiose melts at 225° C and gives $[\alpha]_D^{20}=+14.2°$ initially, which changes in the course of several hours to +34.6°.

NOTES

[1] The simultaneous hydrolysis and acetylation of cellulose was described first by Franchimont [2]. Modifications of the original method are described in references [3, 4, 5, and 6].

[2] This part of the preparation requires some practice in order to obtain uniform results. Several batches may be prepared in this way and combined in the next step, but it is not advisable to work with larger amounts up to this point, as charring may result.

[3] The preparation of the barium methylate solution and additional details for the method are given on page 493.

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4. 2-DESOXYGALACTOSE

Method.—[1, 2, 3] Fifty grams of recrystallized galactal [1] is dissolved in 700 ml of 5-percent cold sulfuric acid, and the solution is kept in the refrigerator at 0° C for 24 hours, after which it is neutralized with 120 g of barium carbonate and the esters are saponified by heating to 60° C. The saponification usually requires about 48 hours of heating. Eight- or ten-gram portions of barium carbonate are added at intervals during this time. The solid material is separated by filtration, and the filtrate is evaporated in vacuo to a thick sirup which is taken up with 50 ml of absolute alcohol and allowed to crystallize. About 40 g of material is obtained.[2]

The crystals are purified by dissolving in water and evaporating the solution to a sirup, which is taken up with three volumes of methyl alcohol and allowed to crystallize, preferably in a slowly rotating flask.

Desoxygalactose melts at 120° to 121° C. In 4-percent aqueous solution, desoxygalactose gives $[\alpha]^{20}_{D}=+40.8°$ initially, which decreases in 5 minutes to a minimum and then increases to +60.5° in about 30 minutes.

NOTES

[1] The preparation of galactal is described on page 532.

[2] The preparation of 2-desoxyglucose and 2-desoxyrhamnose is given by Bergmann, Schotte, and Leschinsky [3], while that of 2-desoxyarabinose and desoxyxylose is described by Levene and Mori [4]. Several natural-occurring desoxy sugars are reported [5, 6, 7].

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5. *l*-FUCOSE (*l*-GALACTOMETHYLOSE)

Method.[1]—[1, 2, 3] The seaweed, *ascophyllum nodosum,* is washed with tap water and any large shells are removed. It is then air-dried and ground to a fine powder. One kilogram of the dried seaweed is added to 8 liters of hot 4-percent sulfuric acid, and the solution is allowed to simmer for 3 hours. The liquid is separated by filtration and the residue is washed with hot water. The filtrate is neutralized with an excess of calcium carbonate, refiltered, and the calcium sulfate washed with water. The mixture is cooled to room temperature and fermented with baker's yeast acclimatized to ferment galactose.[2] When the fermentation is complete, about 100 g of a decolorizing carbon is added; and after standing for several hours, the

solution is filtered and concentrated in vacuo to about 2.5 liters. The precipitated calcium sulfate is separated, and the filtered solution is concentrated to a sirup ($n_D^{20}=1.48$). The sirup is mixed with 1 liter of hot methyl alcohol; the insoluble residue is separated and washed with three 100-ml portions of hot methyl alcohol. The residue is discarded, and the alcoholic extract is purified by adding 600 ml of ether and separating the precipitate by filtration. The solution is concentrated to a thick sirup ($n_D^{20}=1.50$), which is taken up in 200 ml of hot absolute alcohol. The alcoholic solution is filtered and then mixed with 75 ml of phenylhydrazine. After standing for 1 or more days in the refrigerator, the crystalline hydrazone is collected on a filter, washed with absolute alcohol, and dried at 50° C. The hydrazone (100 g) is transferred to a flask containing 50 ml of benzaldehyde and 2 liters of hot water. The mixture is stirred and heated to about 90° C for about 1 hour, after which it is cooled to room temperature. After the addition of 10 g of a decolorizing carbon, the benzaldehyde phenylhydrazone is separated by filtration. The filtrate is extracted three times with 100-ml portions of ether to remove all of the benzaldehyde. The solution is then made acid with acetic acid and concentrated to a sirup of about 80 percent of total solids. This sirup is diluted with about 50 ml of absolute alcohol and seeded with crystalline fucose. After this solution has stood for 1 or more days in the refrigerator, the resulting crystals are separated and washed with absolute alcohol. The yield is about 30 g.

Recrystallization.—The sugar is dissolved in approximately an equal quantity of hot water, and after treatment with a decolorizing carbon, is filtered. The solution is made acid with acetic acid and concentrated in vacuo to a sirup of about 80 percent of total solids ($n_D^{20}=1.490$). This sirup is diluted with 2 ml of absolute alcohol for each gram of sugar and placed in the refrigerator for crystallization to take place. The resulting crystals are collected on a filter and washed with 95-percent alcohol. The mother liquors are concentrated and additional crystals are separated so that nearly all of the sugar is reclaimed. Better purification but lower yields are obtained by crystallizing the sugar from an aqueous solution contained in a flask which is slowly rotated. A solution containing approximately 78 percent of sugar by weight gives a satisfactory crystallization.

In 4-percent aqueous solution *l*-fucose gives $[\alpha]_D^{20}=-152.6°$ initially, which changes in the course of several hours to $-75.9°$.

NOTES

[1] The method is essentially that described by Tollens and coworkers [1] as modified by Clark [2] and by Hockett, Phelps, and Hudson [3].

[2] The fermentation removes mannose and galactose, which are present in certain seaweeds [4].

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323414°—42——31

6. *d*-GALACTOSE

Method.—[1] Fifteen hundred grams of lactose is dissolved in 3,750 ml of hot water containing 75 g of concentrated sulfuric acid. The solution is brought to a boil and then simmered for 2 hours. A thin paste of barium carbonate is then added to the hot solution until it reacts neutral to congo-red paper. The precipitate of barium sulfate is allowed to settle, after which as much as possible of the supernatant liquid is drawn off and filtered. Then the precipitate is placed on the filter and washed with water. The filtrate is concentrated under diminished pressure until it has a weight of about 1,650 g (n_D^{20} between 1.5120 and 1.5125). The very thick sirup is warmed to between 60° and 70° C, and 250 ml of ethyl alcohol is dissolved in it by vigorous shaking. The solution is then poured into a beaker or jar and the remaining sirup is washed from the flask with 500 ml of methyl alcohol. This is best done by adding the methyl alcohol to the flask portionwise and warming and shaking in a water bath. The whole solution is thoroughly mixed, seeded with some pure galactose crystals,[1] and allowed to crystallize, preferably in a slowly rotating flask.

The crystallization is generally complete in about 4 days, after which the crystals are filtered off, washed with a little methyl alcohol, and dried. The yield of the crude sugar is about 27 percent of the lactose taken.[2, 3]

Recrystallization.—The crude galactose is dissolved in an equal weight of hot water, and after the addition of a small quantity of a decolorizing carbon the solution is filtered. A few drops of acetic acid are added, and the solution is evaporated in vacuo to a sirup of 60 percent of total solids ($n_D^{20}=1.442$). The sirup is then seeded with α-*d*-galactose and kept in motion[4] while crystallization proceeds. When a satisfactory crystal growth is obtained (in about 1 day), the crystals are separated either by filtration or by means of a centrifuge. The crystals are washed thoroughly with methyl alcohol. About 50 percent of the sugar is obtained in the first crop, and the remainder may be separated by concentration of the mother liquor.

A more rapid recrystallization can be made by dissolving 200 g of galactose in 100 ml of water, filtering the solution with the addition of about 5 g of a decolorizing carbon, and adding 100 ml of methyl alcohol. The mixture is seeded and stirred while crystallization takes place. After several hours the crystalline galactose is separated by filtration and washed with methyl alcohol. About 75 percent of the original sugar is obtained in the first crop of crystals; the rest of the sugar is reclaimed by concentrating the mother liquor.

In 5-percent aqueous solution, pure α-*d*-galactose has an initial specific rotation, $[\alpha]_D^{20}=+150.7°$, which changes after a number of hours to the equilibrium value, +80.2°.

NOTES

[1] Contamination by dextrose seed must be avoided.

[2] If the hydrolysis is not complete, unchanged lactose may be obtained. Also dextrose may occasionally crystallize simultaneously with the galactose.

[3] Galactose may be prepared from plant gums, such as those from the western larch [2] and by partial fermentation of the hydrolysis products of lactose [3]. A review of methods for the preparation of galactose is given by Harding [4].

[4] If the solution is not kept in motion, the crystals form a solid mass.

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7. GENTIOBIOSE (6-(β-*d*-GLUCOPYRANOSIDO)-*d*-GLUCOSE)

Method.—[1] Gentiobiose is conveniently prepared from the sirupy residue left from the preparation of dextrose from starch. About 4.5 kg of this residue called "hydrol" [1] is dissolved in 30 liters of water, and after the addition of 100 g of calcium carbonate and 2 cakes of baker's yeast the mixture is allowed to stand until fermentation is complete. About 750 g of a decolorizing carbon is added and the solution is filtered. The filtrate is evaporated under reduced pressure to a thick sirup of about 80 percent of total solids ($n_D^{20}=1.490$). The sirup is taken up with 8 liters of a hot mixture of methyl and ethyl alcohols (7 parts of methyl to 1 part of ethyl alcohol). The granular precipitate is extracted several times with methyl alcohol, and the combined extracts are again evaporated to a thick sirup ($n_D^{20}=1.510$). This is mixed with 2 liters of glacial acetic acid and evaporated in vacuo until the solvent ceases to distill. The sirup, weighing 1,300 g and contained in a 12-liter flask, is heated with 500 ml of technical acetic anhydride until a slow visible reaction starts. Twenty grams of anhydrous sodium acetate [2] is introduced, and the mixture is heated with stirring until the reaction becomes vigorous. The source of heat is then removed and *care must be taken to keep the reaction from becoming too violent.* When the reaction has slowed down, more acetic anhydride (500 ml) and sodium acetate (20 g) are added. The addition is repeated until a total of 4,000 ml of the acetic anhydride and 350 g of sodium acetate has been introduced.[3] Heating is then continued for 1 more hour. The solution, after cooling, is poured into 15 liters of water. The insoluble phase is separated by decantation and given several washings with water. The combined water washings are extracted with chloroform to recover any dissolved or suspended product. After evaporation of the chloroform, the residue is combined with the water-insoluble portion and stirred a second time with water. After several hours the insoluble material is separated again and then dissolved in ether and kept at 0° C until crystals of gentiobiose octa-acetate form. This may require 1 or more weeks; hence it is advisable to seed the product with crystalline gentiobiose octa-acetate. Several days after seeding, the crystalline material is separated by filtration, washed with alcohol, and dried.[4] The yield is about 100 g. The crude gentiobiose octa-acetate is recrystallized by dissolving in boiling ethyl alcohol, adding a decolorizing carbon, filtering, and allowing the solution to cool. The recrystallized material weighs 80 g and has a melting point of 193° to 196° C.

The gentiobiose octa-acetate is deacetylated by the barium methylate method of Isbell. Eighty grams is dissolved in 6 liters of dry methyl alcohol with the aid of heating. The solution is cooled to room temperature, 100 ml of 0.6 *N* barium methylate in dry methyl alcohol is added, and the solution is kept at 0° C for 48 hours, after which the barium is precipitated by sulfuric acid or carbon dioxide

and removed by filtration. The solution, free from barium, is concentrated under reduced pressure to a thick sirup which is taken up with methyl alcohol. Crystallization usually takes place in several hours. The crystals when separated weigh about 33 g, and about 15 g more are obtained from the mother liquors.[5]

Recrystallization.—Purification is accomplished by dissolving the material in water, treating with a decolorizing carbon, filtering, and concentrating to a heavy sirup ($n_D^{20}=1.515$) which is dissolved in methyl alcohol [6] and allowed to crystallize.

The isomer obtained in this way has the formula, α-gentiobiose .$2CH_3OH$. The melting point is 86° C, and the initial rotation, $[\alpha]_D^{20}=+21.4°$, changes to the equilibrium value, $[\alpha]_D^{20}=+8.7°$ (as alcoholate).

NOTES

[1] "Hydrol" may be obtained from the concerns manufacturing dextrose.

[2] Anhydrous sodium acetate is prepared by fusing the hydrate in an iron crucible. See p. 488, note 1.

[3] The reaction takes place much less violently as the addition proceeds, and the materials may be added at short intervals after the third or fourth addition.

[4] The alcohol washings should be kept separate from the mother liquor, which usually does not yield any further material.

[5] Gentiobiose may be prepared from gentian root [2, 3, 4] or synthesized by the method of Reynolds and Evans [5].

[6] Methyl alcohol is the only alcohol which should be used, since the sugar crystallizes as the difficultly soluble methyl alcoholate.

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8. 4-GLUCOSIDOMANNOSE, (4-(β-*d*-GLUCOPYRANOSIDO)-*d*-MANNOSE)

Method.—[1,2] Six grams of octaacetyl-4-glucosidomannose [1] is dissolved in 150 ml of absolute methyl alcohol, and the solution treated with 5 ml of about 0.5 *N* barium methylate solution.[2] After 24 hours the barium is removed by adding an equivalent quantity of sulfuric acid [3] and filtering. The filtered solution is evaporated in vacuo to a thick sirup which is taken up with 10 ml of ethyl alcohol. About 2.4 g of crystalline 4-glucosidomannose separates in the first crop, and a small amount (0.2 g) is obtained from the mother liquor. The sugar crystallizes in the alpha modification as a monohydrate which melts at 137° C.[4]

In 4-percent aqueous solution, 4-(β-*d*-glucosido)-α-*d*-mannose hydrate gives $[\alpha]_D^{20}=+14.7°$ initially, which changes in the course of several hours to +5.9°.

NOTES

[1] The preparation of octaacetyl-4-glucosidomannose is given on page 501.

[2] The barium methylate solution is prepared by adding 125 g of powdered barium oxide to 500 ml of absolute methyl alcohol. After standing for several hours, the solution is filtered. It should be kept in a bottle protected from moisture and carbon dioxide.

[3] Since moisture or acids in the original sirup will decompose the barium methylate, it is well to test the deacetylated mixture to see if an excess of barium methylate

is present. This may be done by diluting a few milliters with water and adding several drops of phenolphthalein solution. A definite red color indicates a sufficient excess. If the test is not positive, add more barium methylate solution to the deacetylation mixture and allow 24 hours more for the deacetylation to be completed.

[4] Glucosidomannose has been made by the oxidation of cellobial with perbenzoic acid [3,4]. The method as applied to *d*-talose is given on page 479.

REFERENCES

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9. α-*d*-GULOSE.$CaCl_2.H_2O$

Method.—[1] Pure *d*-gulonic gamma lactone is reduced by sodium amalgam in a 6-liter stainless-steel pot equipped with a strong mechanical stirrer with broad metal paddle and cooled by a mixture of ice and salt. The lactone (90 g) is dissolved in 800 ml of water and 150 ml of 95-percent ethyl alcohol, and cooled to about −10° C. About 14 ml of 20-percent sulfuric acid is added to the solution, followed by 1,500 g of 3-percent sodium amalgam, which is added (in 1 portion) with vigorous stirring.[1] Twenty-percent aqueous sulfuric acid is added to the mixture at such rate as to maintain the solution acid at about pH 3.[2] After the sodium amalgam has reacted, the mixture is transferred to a separatory funnel and the mercury is separated. The solution is returned to the pot used for reduction, and after cooling to about −10° C, a second 1,500-g portion of sodium amalgam is added and the reduction continued while the solution is kept acid and cold as before. When the amalgam is spent, the mixture is again transferred to a separatory funnel and the mercury is separated. The cold solution is filtered to remove the crystalline sodium sulfate, and sodium hydroxide is added to the filtrate in sufficient quantity to neutralize the excess acid and to saponify any gulonic lactone. After the lactone is saponified, as shown by an alkaline reaction after standing for 15 minutes, the solution is acidified with dilute sulfuric acid and evaporated under reduced pressure until the formation of crystalline sodium sulfate causes difficulty with further evaporation. The concentrated liquor is mixed with 2 volumes of ethyl alcohol and allowed to stand for several hours, preferably in a refrigerator. The insoluble salts are separated from the alcoholic solution by filtration and then washed with methyl alcohol. The alcoholic solution is evaporated to a thick syrup. This is mixed with 500 ml of hot ethyl alcohol, which results in the precipitation of most of the salt in the form of an amorphous residue. Most of the sugar is found in the alcoholic solution; that which remains in the residue may be separated by dissolving the residue in water and reprecipitating the salt by the addition of alcohol. The combined alcoholic solutions are evaporated in vacuo to a heavy sirup. The crude gulose may be purified by means of its phenylhydrazone or the product may be converted to *d*-gulose calcium chloride without further purification.[3] The calcium chloride compound is prepared by adding in aqueous solution approximately 1 molecular equivalent of calcium chloride. The aqueous solution is evaporated in vacuo

to a thick sirup, from which crystalline gulose $CaCl_2.H_2O$ or $(gulose)_2$-$CaCl_2.H_2O$ crystallizes readily. The crystalline massecuite is diluted with a small quantity of ethyl alcohol before filtration, and the crystals are washed with ethyl alcohol. After further concentration the mother liquors give additional product. In all, about 70 g of gulose.$CaCl_2.H_2O$ is obtained.

In 6.8-percent aqueous solution, α-*d*-gulose.$CaCl_2.H_2O$ gives $[\alpha]^{20}_{D}=+37.1°$, changing to an equilibrium value of $-10.0°$.

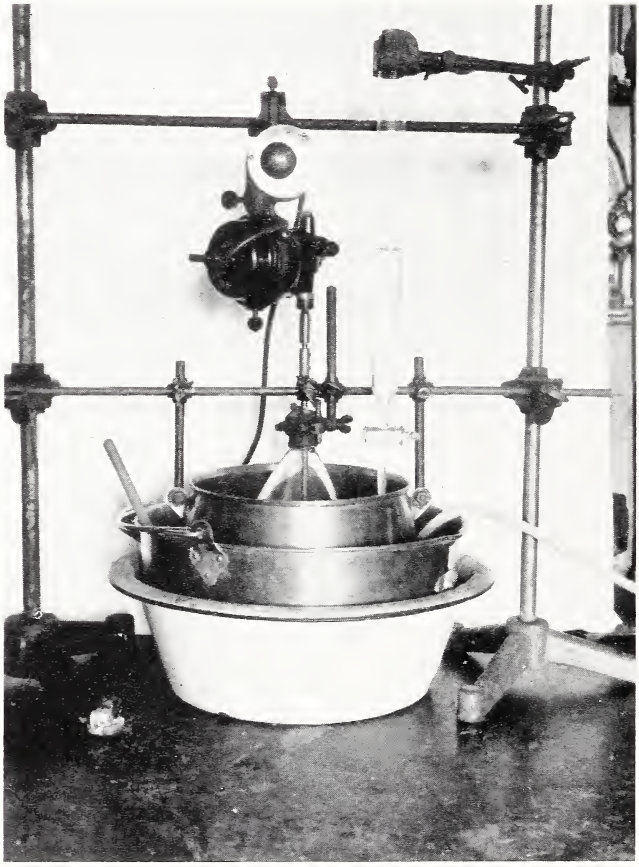

FIGURE 110.—*Apparatus used for the reduction of sugar lactones with sodium amalgam.*

NOTES

[1] Best results are obtained with hard amalgam in pieces about ½ cm in diameter.

[2] The reaction can be followed by using thymol-blue or congo-red paper as an outside indicator. Thymol-blue paper should turn pink and congo-red paper should turn purple.

[3] In order to obtain gulose.$CaCl_2.H_2O$ free from sodium salts, it is necessary to remove all sodium salts before adding the calcium chloride. This is most readily accomplished by the intermediate preparation of the phenylhydrazone.

REFERENCES

[1] H. S. Isbell, BS J. Research **5**, 741 (1930) RP226.

10. LACTOSE (4-(β-*d*-GALACTOPYRANOSIDO)-*d*-GLUCOSE)

Method.—This disaccharide is available at a low price as a commercial product which is prepared from the whey obtained from the manufacture of cheese. Details of the method are described by Nabenhauer [1] and are included in the United States Dispensatory [2]. The usual commercial product is α-lactose.H_2O, but the much more soluble anhydrous β-lactose is also available in large quantities. Methods for preparing β-lactose are reviewed by Bell [3].

Recrystallization.—One kilogram of lactose hydrate is dissolved in 750 ml of hot water. After the addition of 20 g of a decolorizing carbon the hot solution is filtered. The clear filtrate is allowed to cool slowly with stirring. After several hours at room temperature the crystals which separate are collected on a filter and washed, first with a mixture of equal volumes of water and methyl alcohol, and then with undiluted methyl alcohol. The first crop of crystals is about 65 percent of the crude product. The remaining sugar is reclaimed by evaporating the mother liquor in vacuo.

Crystalline α-lactose hydrate in 7.6-percent aqueous solution gives $[\alpha]_D^{20} = +85.0°$ initially, changing in several hours to $+52.6°$.

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11. LACTULOSE (4-(β-*d*-GALACTOPYRANOSIDO)-*d*-FRUCTOSE)

Method.—[1] A solution containing 1,200 g of commercial lactose[1] in 6 liters of water saturated with calcium hydroxide at 35° C is kept at approximately 35° C for several days or until the optical rotation shows no further change.[2] Subsequently the solution is concentrated in vacuo until the weight is reduced to about 1,500 g. The resulting residue, which contains considerable crystalline lactose, is diluted with 1,500 ml of methyl alcohol and allowed to stand in a cold place for several days for the crystallization of any unchanged lactose. The crystalline lactose (about 800 g) is separated by filtration and washed with 450 ml of methyl alcohol. The filtrate is concentrated in vacuo to a sirup which is diluted with 600 ml of water and evaporated again to remove the alcohol. The alcohol-free solution is diluted with water to a volume of 2.5 liters, and the quantity of bromine necessary to oxidize the aldoses to aldonic acids is ascertained in the following manner:

A 5-ml sample of the soution is placed in a 200-ml Erlenmeyer flask and 5 ml of 0.1 *N* iodine is added from a burette; 7.5 ml of 0.1 *N* sodium hydroxide is then added dropwise. The addition of alkali and iodine is repeated until 30 ml of iodine and 45 ml of alkali have been added. The solution is acidified with 10 ml of 1 *N* hydrochloric acid and the excess iodine titrated with 0.1 *N* sodium thiosulfate using starch indicator. The iodine titration of the sample is the difference between the quantity of 0.1 *N* iodine added and the back titration.[3] If the volume of the sugar solution is 2.5 liters, the bromine in hydrogen equivalents [4] is one twentieth of the iodine titration of the 5-ml sample. Before adding the bromine, sufficient calcium carbonate is added to combine with the acids formed by the oxidation;

this requires 75 g for each equivalent of bromine. The calculated quantity of bromine is then placed in a dropping funnel and added drop by drop over a period of several hours while the solution is mixed with a mechanical stirrer. After all of the bromine has been added, the mixture is allowed to stand for several hours. About 20 g of a decolorizing carbon is then added and the solution is filtered. The bromides in the filtrate are precipitated by mixing with finely powdered silver sulfate,[5] using 160 g for each equivalent of bromine. The resulting precipitate is separated by filtration and washed with water. The bromide-free filtrate is then treated with hydrogen sulfide to precipitate the excess silver. The resulting silver sulfide is removed by filtration, and the filtrate is then evaporated to a volume of about 1,500 ml in vacuo to remove the excess hydrogen sulfide. The solution is neutralized with calcium carbonate, filtered and evaporated to a sirup of approximately 75 percent of total solids ($n_D^{20}=1.477$). The sirup is mixed with 1,200 ml of hot methyl alcohol and separated into methyl alcohol-soluble and alcohol-insoluble material. The alcohol-insoluble material is given a second and a third extraction with 300-ml portions of methyl alcohol, and it is then discarded. The combined alcoholic extract is diluted with 900 ml of 95-percent ethyl alcohol, and the resulting amorphous precipitate is allowed to settle. The clear alcoholic solution is decanted, and the gummy residue is extracted with 100 ml. of methyl alcohol. The residue is discarded. The alcoholic solution is combined with the alcoholic extract previously obtained, and the mixture is then evaporated in vacuo to a sirup of about 85 percent of total solids ($n_D^{20}=1.503$). This sirup is mixed with 300 ml of methyl alcohol, and then absolute ethyl alcohol is added in sufficient quantity (about 200 ml) to saturate the sirup without giving two liquid phases. The alcoholic solution is seeded with crystalline lactulose and allowed to stand for crystallization. After several days the crystalline lactulose is separated by filtration. The mother liquor after concentration, extraction with methyl alcohol, and subsequent evaporation yields additional lactulose. A total of about 180 g of crystalline lactulose is obtained.

Recrystallization.—One hundred grams of crude lactulose is dissolved in hot water and the solution is filtered, using a small quantity of a decolorizing carbon. The filtrate is evaporated to a thick sirup containing about 85 percent of total solids ($n_D^{20}=1.503$). The sirup is mixed with 200 ml of warm methyl alcohol and after cooling, the solution is seeded with crystalline lactulose. Crystallization takes place in the course of several hours, during which time the mixture is preferably kept in gentle motion. The crystals are collected on a filter and washed with methyl alcohol. About 75 g of crystalline lactulose is obtained in the first crop. The rest of the sugar is reclaimed by concentrating the mother liquor.

Pure lactulose melts at 160° C and in 4-percent aqueous solution gives $[\alpha]_D^{20}=-11.9°$ initially, changing in several hours to $-50.7°$ [2].

NOTES

[1] For the preparation of lactose see page 467.

[2] In a typical experiment the optical rotatory change as observed in a 2-dm tube was as follows:

Time	Observed rotation
Hours	°*S*
0	53. 0
25	31. 0
71	30. 1

[3] If the titration requires less than 4 ml of the thiosulfate, sufficient iodine and sodium hydroxide were not added and the analysis must be repeated, using more of the reagents.

[4] For each equivalent, use 26 ml of bromine.

[5] In large-scale preparations oxalic acid and lead carbonate can be used in place of silver sulfate. The amount of oxalic acid equivalent to the bromine used is added first and then an equivalent quantity of lead carbonate. The resulting insoluble salts are separated and any bromide which remains in the filtrate is removed by precipitation with silver sulfate, after which the procedure is the same as that given above.

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12. *d*-LYXOSE

Method.[1]—[1] A mixture of 225 g of calcium galactonate.$5H_2O$[2], 20 g of barium acetate monohydrate, and 10 g of ferric sulfate (crystalline) is added to 3 liters of boiling water. After the mixture is cooled to 35° C, 120 ml of 30-percent hydrogen peroxide [3] is added. A vigorous reaction begins in a few minutes. The solution is cooled so that the temperature does not exceed 50° C. When the solution turns dark brown, it is cooled to 40° C and a second 120-ml portion of hydrogen peroxide is added. After the ensuing reaction is complete, about 20 g each of a decolorizing carbon and of calcium carbonate are added and the solution is filtered. The filtrate is concentrated in vacuo to a sirup of about 80 percent of total solids ($n_D^{20}=1.490$). The sirup is mixed with 300 ml of methyl alcohol and then with 600 ml of hot ethyl alcohol. The resulting precipitate is separated by filtration and washed, first on the filter with 100 ml of ethyl alcohol; then it is transferred to a beaker and mixed with 200 ml of ethyl alcohol, after which it is returned to the filter and finally washed with another 100 ml of alcohol. The insoluble residue is discarded. The filtrate is evaporated in vacuo to a thick sirup ($n_D^{20}=1.51$, or about 90 percent of total solids), which is extracted with 200 ml of hot absolute alcohol. The residue in the distillation flask is extracted with three 200-ml portions of hot isopropyl alcohol. The residue is discarded. The alcoholic extracts are combined and allowed to stand at room temperature until the supernatant liquid is clear. The clear liquid is decanted from the sirupy residue[4], and after the addition of a few drops of acetic acid the solution is evaporated in vacuo to a sirup which is then seeded with β-*d*-lyxose and placed in a desiccator over calcium chloride for crystallization to take place.[5] After several days the crystals are collected on a filter, washed with absolute alcohol, and dried. The yield is about 30 g. The mother liquor is concentrated in vacuo, the sirup is extracted with absolute alcohol, and the solution is evaporated to give a second crop.

Recrystallization.—An aqueous solution containing a few milliliters of acetic acid and 100 g of crude lyxose is concentrated in vacuo at 40° C to a sirup of 90 percent of total solids. This sirup is mixed with 200 ml of hot absolute ethyl alcohol and the hot solution is filtered, using about 5 g of a decolorizing carbon. After cooling and seeding, about 60 g of crystalline lyxose is obtained.

Usually β-*d*-lyxose crystallizes more readily than α-*d*-lyxose, although either isomer may be obtained by the same procedure.

In 4-percent aqueous solution β-*d*-lyxose gives $[\alpha]_D^{20} = -72.6°$ initially, changing in 1 or 2 hours to $-13.8°$.

NOTES

[1] The method described is a considerable improvement over that originally described by Ruff and Ollendorf [2]. The sugar may also be prepared from *d*-xylose by application of the glycal method [3] or by the pyridine rearrangement from *d*-xylonic acid [4].

[2] The method used for the preparation of calcium galactonate is similar to that given on page 524.

[3] If the hydrogen peroxide is not fresh, it should be analyzed and the volume equivalent to that given should be used.

[4] When considerable residue is obtained at this point, it should be extracted with absolute ethyl or isopropyl alcohol in order to recover the lyxose which is present.

[5] In order to obtain a satisfactory crystallization it is necessary to keep the amount of water in the sirup as low as possible. If the product fails to crystallize, usually crystallization can be effected by evaporating the alcoholic solution a second time, dissolving the residue in absolute alcohol, and precipitating the impurities with isopropyl alcohol.

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13. MALTOSE (4-(α-*d*-GLUCOPYRANOSIDO)-*d*-GLUCOSE)

The technical grade of maltose usually contains considerable quantities of dextrins, which must be removed by precipitation with alcohol in order that a pure product be obtained on recrystallization. If the technical maltose is not available, the following directions, which are essentially those given by Harding [1] and based on the method of Herzfeld [2], may be used to prepare maltose from starch.

Method.—Twenty-five hundred grams of soluble starch[1] is added to 20 liters of hot water and the mixture is stirred until complete solution has taken place. After the solution is cooled below 50° C, 100 g of barley flour (or coarsely ground barley meal) is added and the solution allowed to stand for 20 hours. The unfiltered solution is then concentrated under reduced pressure to a volume of about 3 liters.

This solution (or one prepared by dissolving 2,500 g of technical maltose in water and evaporating the solution to a volume of 3 liters) is mixed with 5.5 liters of alcohol and stirred for ½ hour with a mechanical stirrer. The insoluble material is allowed to settle and the alcoholic solution decanted. The gummy residue is mixed with 3 liters of alcohol. The mixture is allowed to settle, and the alcoholic solution is separated by decantation. The residue is given a third extraction with 2 liters of alcohol, the alcohol is separated, and the residue discarded.

The combined alcoholic extracts are evaporated under reduced pressure to a volume of about 5 liters. The solution is treated with a decolorizing carbon, filtered, and the filtrate is then evaporated to a thick sirup (volume less than 1 liter). This is diluted with ethyl alcohol (containing 1 percent of nitric acid[2] by volume) until an amorphous gum appears. Seed crystals are then added and the solution is placed in a refrigerator for a day while crystallization takes place. The solution is diluted with alcohol (containing nitric acid) from time to time to prevent solidification. The crystals are separated by filtration and washed with alcohol. From the mother liquors, additional material may be obtained.

Recrystallization.—The maltose may be recrystallized by dissolving the crystals in hot water, evaporating the solution in vacuo to a thin sirup which is taken up with ethyl alcohol, and allowing the sugar to crystallize, preferably in a slowly rotating flask. The sugar is obtained as β-maltose.H_2O, which has an initial rotation in 4-percent aqueous solution of $[\alpha]_D^{20}=+111.7°$ and an equilibrium rotation of $+130.4°$.

NOTES

[1] Technical maltose may be purchased for about 50 cents a pound. Soluble starch may be prepared by mixing a good grade of commercial starch with sufficient 7.5-percent hydrochloric acid to cover the starch. After the mixture stands for about 1 week at room temperature, the acid is washed out and the resulting soluble starch is air-dried.

[2] The nitric acid assists in removing colored and opalescent material from the solutions.

REFERENCES

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14. *d*-MANNOSE

Method.[1]—[1, 2, 3] One kilogram of screened ivory-nut shavings [2] is mixed with 1 kg of cold 75-percent sulfuric acid (430 ml of concentrated sulfuric acid and 250 ml of water). The material is triturated until the sulfuric acid is uniformly distributed, and is allowed to stand until the next day, preferably at about 35° C. The mass is then dissolved in 10 liters of water and the solution is filtered through cheesecloth. The filtrate is heated to boiling for 6 hours while the volume is maintained approximately constant. The hot liquid is then neutralized with barium carbonate, and after the addition of 200 g of decolorizing carbon the barium sulfate is separated by filtration. The filtrate is evaporated in vacuo to a sirup of about 85 percent of total solids ($n_D^{20}=1.503$). This sirup is thoroughly mixed with 1 liter of warm methyl alcohol, after which the solution is diluted with 2 liters of isopropyl alcohol. This results in the precipitation of some gummy amorphous material, which is separated by decantation. The larger part of the mannose is in the alcoholic extract; that in the gummy residue is separated by triturating the gum with 250 ml of methyl alcohol and then adding 500 ml of isopropyl alcohol. The mixture is allowed to settle and the insoluble residue is separated from the alcoholic extract. The residue thus obtained is given a second treatment with methyl and isopropyl alcohols, and the alcoholic extracts are combined. After the addition of about 50 g of decolorizing carbon, the solution is filtered and evaporated in vacuo to a sirup of about

60 percent of total solids ($n_D^{20}=1.442$). This sirup is taken up with 250 ml of glacial acetic acid and seeded with α-*d*-mannose. In the course of several days at room temperature, 200 g of crystalline mannose separates.[3] This is collected on a filter and washed with a mixture containing 3 parts of ethyl alcohol and 1 part of methyl alcohol. A second crop of 150 g of crystalline mannose is obtained by evaporating the mother liquors to a thick sirup containing about 85 percent of total solids ($n_D^{20}=1.503$). This sirup is taken up in glacial acetic acid, seeded with α-*d*-mannose, and allowed to stand in the refrigerator for several days, after which the crystals are separated in the usual manner.

Recrystallization.—One hundred grams of crude mannose is dissolved in 100 ml of water. After the addition of a few drops of acetic acid and 5 g of a decolorizing carbon, the solution is filtered and evaporated in vacuo to a heavy sirup ($n_D^{20}=1.511$). The sirup is mixed with 50 ml of warm methyl alcohol, followed by 200 ml. of a mixture containing equal volumes of methyl and isopropyl alcohols. The sirup is decanted from any gummy material, filtered if necessary, and then seeded with about 0.5 g of α-*d*-mannose and allowed to crystallize, preferably while kept in motion. In the course of 1 or more days about 75 g of the crystalline sugar separates. By concentrating the mother liquor and repeating the process, nearly all the mannose can be separated in the crystalline state.

In 4-percent aqueous solution α-*d*-mannose gives $[\alpha]_D^{20}=+29.3°$ initially, changing in the course of several hours to an equilibrium value of $+14.2°$.

NOTES

[1] The method is similar to that described by Clark [1] but differs in that any gums are precipitated with a mixture of methyl and isopropyl alcohol. This step (introduced by Isbell) results in a product which crystallizes readily. Hudson and Jackson recommend the intermediate preparation of α-methyl mannoside [3].

[2] The ivory-nut shavings may be purchased from the Button Machinery Co., 11th, Grand and Adams Sts., Hoboken, N. J.

[3] If the hydrolysis is incomplete or if the gummy material is not separated, the mannose may crystallize very slowly.

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15. MELEZITOSE (*d*-GLUCOSIDO-SUCROSE)

Occurrence.—The trisaccharide, melezitose, occurs in a manna that forms upon the Douglas fir, jack pine (*Pinus Virginiana* Mill), and other trees as the result of the activities of a reddish-brown soft-scale insect. During periods of drought, bees collect the manna or honey dew in sufficient quantity to change the character of the honey, making it unsuitable for maintaining the bees but providing a source of melezitose [1] [1]. Melezitose is not fermented by baker's yeast and does not reduce Fehling solution. The analysis of melezitose-containing honey shows a large increase in reducing sugars by acid inversion in comparison with the increase in reducing sugars by invertase hydrolysis.

Method.[2]—The honey containing crystalline melezitose is cut into pieces and coarsely ground in a meat grinder. One liter of ethyl

alcohol is added to each 15 pounds of honey and the mixture is allowed to stand overnight, after which the solid material is separated on a basket centrifuge and the cake is washed with 80-percent alcohol. On account of the difference in the density of the wax and sugar, the sugar collects as a layer on the outer edge of the basket. The wax and lighter impurities collect as an inner layer. The sugar and wax layers are separated mechanically. The outer layer, which is largely sugar, is mixed with 80-percent aqueous alcohol to form a thin paste which is passed through a coarse sieve (14 mesh), whereupon the larger wax particles are retained on the screen while the grains of sugar pass through. The sugar in the alcoholic suspension is separated on a centrifuge. The cake is dissolved in hot water and clarified with a decolorizing carbon. The resulting solution usually contains colloidal material, which is removed by adding a small quantity of milk of lime followed by an equivalent quantity of phosphoric acid. The cold neutral solution is filtered and evaporated in vacuo. As the evaporation proceeds, crystalline melezitose forms. When sufficient crystals are present, the evaporation is stopped and the crystals are separated. The mother liquors yield additional crystalline sugar by further evaporation. A small quantity of melezitose can be extracted from the wax by solution in cold water and subsequent crystallization. The yield varies widely with different samples of honey.[3] In 4-percent aqueous solution melezitose gives $[\alpha]_D^{20}=+88.2°$.

NOTES

[1] A sample of wax and crystals collected from in front of a hive of bees was submitted by the Bureau of Entomology, U. S. Department of Agriculture, to the National Bureau of Standards for analysis. The analysis showed that the sample contained over 60 percent of melezitose.

[2] This method was worked out by Hudson and Isbell at the National Bureau of Standards but has not heretofore been published.

[3] From 250 kg of melezitose honey, Isbell and Hudson, working in the Polarimetry Section of the National Bureau of Standards, obtained 13 kg of crystalline melezitose.

REFERENCES

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16. MELIBIOSE (6-(α-*d*-GALACTOPYRANOSIDO)-*d*-GLUCOSE)

Method.[1]—[1] Two hundred and fifty grams of raffinose [2] is dissolved in 2½ liters of water containing a cake of baker's yeast [3] (5 to 10 g), 50 g of calcium carbonate, and 50 ml of nutrient solution.[4] The fermentation is allowed to take place for 3 or 4 days.[5] After the addition of 75 g of a decolorizing carbon, the solution is filtered. The filtrate is treated with 25 g of basic lead acetate, and the lead is removed by treating with hydrogen sulfide and filtering off the lead sulfide. The filtered solution is evaporated to a sirup of approximately 80 percent of total solids ($n_D^{20}=1.490$), after which the sirup is taken up in 100 ml of glacial acetic acid and nucleated with melibiose hydrate. Crystallization [6] usually takes place in several days at 0° C. The crystals are separated and washed, first with acetic acid and then with 95-percent alcohol. The yield is about 100 g.

Recrystallization.—A solution of 100 g of crude melibiose in 70 ml of hot water is treated with 2 g of a decolorizing carbon and filtered. The filtrate is cooled, mixed with 150 ml of glacial acetic acid, and

seeded with melibiose hydrate. After standing for several days in the refrigerator, about 50 g of melibiose hydrate crystallizes from the solution. The crystals are separated and washed, first with glacial acetic acid, and then with 95-percent ethyl alcohol. Nearly all the sugar can be reclaimed by concentrating the mother liquors and crystallizing from aqueous acetic acid.

The sugar crystallizes in the beta modification containing 2 molecules of water of crystallization. In 4-percent aqueous solution, β-*d*-melibiose. $2H_2O$ gives $[\alpha]_D^{20}=+111.7°$ initially, which changes in the course of several hours to $+129.5°$.

NOTES:

[1] Bau [2] describes a similar method but separates the melibiose as the barium saccharate. A review of the literature is given by Harding [3].

[2] Raffinose may be obtained as described on page 475.

[3] Brewer's yeast (bottom yeast) must not be used as it contains an enzyme which hydrolyzes the melibiose [2].

[4] A stock nutrient solution of the following composition may be used:

Salt	g/liter
$NaNO_3$	100
KH_2PO_4	8.0
$MgSO_4.7H_2O$	6.6

[5] In a typical experiment the rotation dropped from $+52.85°$ to $+40.1°$S. The reaction should be stopped when a proportionate change has been observed.

[6] If crystallization does not take place, it can sometimes be induced by adding a small quantity of water. However, it is sometimes necessary to purify the sugar further by converting it to the crystalline acetate, which may be deacetylated to give a nearly pure product that crystallizes readily. The acetylation and deacetylation are conducted essentially as described for gentiobiose on page 463.

REFERENCES

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17. NEOLACTOSE (4-(β-*d*-GALACTOPYRANOSIDO)-*d*-ALTROSE)

Method.—[1, 2] Heptaacetylneolactose[1] is deacetylated by the barium methylate method of Isbell[2] as follows: Eighty-four grams of the β-heptaacetylneolactose is dissolved in 1,500 ml of dry methyl alcohol; the solution is cooled in an ice bath, after which 75 ml of 0.5 *N* barium methylate in dry methyl alcohol is added and the solution is kept in a cold place (0°C) for 20 hours. The barium is removed with an equivalent quantity of sulfuric acid or by treatment with carbon dioxide, and the solution is concentrated in vacuo to a thick sirup, which is dissolved in about 2 volumes of methyl alcohol and allowed to stand for several days in a refrigerator. Spontaneous crystallization usually takes place during this time, but if not, the solution must be nucleated with crystalline material[3]. The crystals are separated by filtration and washed with methyl alcohol. The yield is close to the theoretical.[4] The crystals are purified by dissolving them in water, evaporating the solution under reduced pressure to a thin sirup,

dissolving the sirup in methyl alcohol, and allowing crystallization to take place, preferably in a slowly rotating flask.

The pure material has a melting point of 190° C and exhibits a small mutarotation from an initial value of $[\alpha]_D^{20}=+33.8°$ to an equilibrium value $[\alpha]_D^{20}=+35.5°$.

NOTES

[1] Heptaacetylneolactose is prepared from chloro-heptaacetylneolactose (page 502) by the method described for heptaacetyl-4-(β-*d*-glucosido)-*d*-mannose on page 491.

[2] Additional details for carrying out this method of deacetylation are described on page 464.

[3] Seed crystals may be obtained by rubbing up a small quantity of the sirup with acetone and alcohol.

[4] In a typical experiment 31 g was obtained from the first crystallization and the mother liquors yielded 7 g additional.

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18. RAFFINOSE (*d*-GALACTOSIDO-SUCROSE)

Commercial source.—Since the trisaccharide, raffinose, is commercially available at a reasonable price, details of a preparatory method are not given. The sugar is produced in large quantities as a by-product of the "Barium Process" for the recovery of sucrose from beet molasses and may be obtained from The Great Western Sugar Co., Denver, Colo. Methods for the preparation of raffinose are given in references [1, 2, 3].

Recrystallization.—Three hundred grams of raffinose is dissolved with 200 ml of water. After the addition of a small quantity (5 g) of a decolorizing carbon, the hot solution is filtered and the residue on the filter is washed with 25 ml of hot water. The filtered solution is mixed with 200 ml of ethyl alcohol and seeded with crystalline raffinose. The mixture is allowed to cool slowly while being stirred. After several hours the resulting crystals are separated by filtration and are washed, first with a mixture of equal volumes of water and ethyl alcohol, and then with 95-percent ethyl alcohol. The first crop of crystals constitutes about 75 percent of the total sugar. The sugar in the mother liquor is reclaimed by evaporating the solution in vacuo. In 10-percent aqueous solution raffinose pentahydrate gives $[\alpha]_D^{20}=+105.2°$. It does not exhibit mutarotation.

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19. *l*-RHAMNOSE (*l*-MANNOMETHYLOSE)

Method.—[1, 2] Five hundred grams of lemon flavine [1] is boiled with 4 liters of 0.5-percent (by weight) sulfuric acid for 5 hours,[2] after which the hot solution is then filtered through a large Büchner funnel. The acid in the hot filtrate is neutralized by the cautious addition of barium carbonate. The precipitate of barium sulfate is removed by filtration and the filtrate is then treated with 400 g of a decolorizing

carbon, allowed to stand overnight, filtered, and evaporated to a 75-percent sirup ($n_D^{20}=1.477$) which crystallizes readily.[3] The crystals are separated and washed, first with 1:1 aqueous ethyl alcohol and then with 95-percent ethyl alcohol. The yield is about 90g. A review of the literature is given by Harding [3].

Recrystallization.—Three parts of rhamnose hydrate are dissolved with 2 parts of hot water. After a small quantity of a decolorizing carbon is added, the solution is filtered and seeded with crystalline rhamnose. Crystallization takes place in the course of several hours at room temperature, during which time the mixture is preferably kept in motion. The crystals are separated and washed, first with 75-percent and then with 95-percent aqueous alcohol. The first crop of crystals is about 60 percent of the crude product. By concentrating the mother liquors in vacuo, additional crystalline sugar is obtained.

The modification of the sugar obtained under these conditions is α-*l*-rhamnose monohydrate. In 4-percent aqueous solution this substance exhibits $[\alpha]_D^{20.2}=-8.6°$ and at equilibrium $+8.2°$.

NOTES

[1] Lemon flavine is a commercial yellow dyestuff prepared from black oak bark and may be obtained from J. S. Young and Company, Hanover, Pa.

[2] The solution may be heated over a direct flame, provided a suitable stirring device is used. Foaming may be reduced by the occasional addition of an antifoam agent, such as capryl alcohol.

[3] If crystallization does not take place spontaneously, add seed crystals. If crystallization still does not commence, extract the aqueous solution with 95-percent alcohol, discard the residue, and evaporate the extractions to a sirup of about 75 percent of total solids, seed, and allow to stand until crystallization takes place.

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[2] C. F. Walton, Jr., J. Am. Chem. Soc. **43,** 127 (1921).
[3] T. S. Harding, Sugar **25,** 82 (1923).

20. *d*-RIBOSE

Method.—[1, 2, 3, 4] The following specific directions for the preparation of ribose have been found convenient and effective in this laboratory.

Hydrolysis of nucleic acid.—Five hundred grams of commercial yeast nucleic acid,[1] 100 g of magnesium oxide, and 3 liters of distilled water are placed in a 4-liter Pyrex beaker and mixed until a uniform, smooth suspension is obtained free from lumps.[2] The mixture in the 4-liter beaker or in a 5-liter short-necked flask [3] is placed in an autoclave and heated to 145° C (60 pounds steam pressure) for 4 hours with continuous stirring.[4] The maximum working range of temperature lies between approximately 120° and 155° C [5].

The pressure in the autoclave is then reduced as quickly as possible without causing the reaction mixture to boil over. As soon as the pressure is reduced, the autoclave is opened and the boiling-hot reaction mixture filtered through a little decolorizing carbon on a large Büchner funnel into a 4-liter filtering flask.[5] The copious precipitate of magnesium-containing phosphates is packed down and washed with 1 to 1½ liters of boiling water, making the total volume of filtrate and washings between 3.5 and 4 liters.

Separation of guanosine.—The filtrate from the hydrolysis of nucleic acid is allowed to stand overnight in a stoppered 4-liter Erlenmeyer flask at room temperature, or preferably in the icebox to permit the guanosine to crystallize out as completely as possible.

The crude guanosine is filtered off and washed on the filter with cold water followed by alcohol to facilitate drying. The yield is 70 to 80 g of crude air-dried guanosine.

Purification of guanosine.—The crude guanosine is purified by recrystallization from a 4-percent solution in water. Two and one-half liters of distilled water is heated to boiling and to this is added 100 g of crude guanosine. The mixture is stirred vigorously to hasten solution and when dissolved it is filtered immediately [6] through a little decolorizing carbon [7] on a large Büchner funnel. The filtrate is cooled and allowed to stand overnight, whereupon crystalline guanosine separates. The product is collected on a filter, washed with water and then with alcohol, and dried at a low temperature (about 35° C). Usually one recrystallization provides sufficient purification. However, if the crystals in the magma do not show clean-cut end faces, or if the magma appears somewhat gelatinous, a second recrystallization after filtration through carbon may be desirable.

Separation of adenosine.—From the filtrate obtained from the crude guanosine, adenosine may be precipitated without further purification by the addition of picric acid, or if desired, a preliminary treatment may be given to remove the small excess of magnesia as follows:

To the filtrate obtained from the crude guanosine is added a solution of about 2 g of ammonium phosphate, followed by dilute barium hydroxide to about pH 9, or as long as a precipitate continues to be formed. The solution is filtered. The filtrate is immediately treated with dilute sulfuric acid in sufficient quantity to precipitate any barium salts, which are then separated by filtration. The addition of dilute sulfuric acid to the filtrate is continued until the solution remains just acid to congo red. At this point a nearly saturated solution of picric acid in hot 90-percent alcohol is added until no more immediate precipitate is formed. Approximately 50 g of picric acid is required. The precipitate is filtered, washed with water slightly acidified with picric acid, then with alcohol, and finally is air-dried. About 100 to 115 g of air-dried crude adenosine picrate containing some cytidine picrate is obtained.

Purification of adenosine picrate.—The crude adenosine picrate may be sufficiently purified by one or two recrystallizations from hot water using a little decolorizing carbon in the filtration. The crude wet adenosine picrate is taken from the filter, and without drying, is added immediately to boiling water [6] until the solution is nearly saturated, whereupon it is filtered at once through washed carbon [7] on a large Büchner funnel. The solution is allowed to crystallize overnight, and the crystals are filtered, washed with water and alcohol, and air-dried. Adenosine picrate may be hydrolyzed directly without removing the picric acid.

Hydrolysis of guanosine.—One hundred grams of recrystallized guanosine is dissolved in 10 liters of approximately 0.1 *N* sulfuric acid at the boiling temperature, and hydrolysis at boiling temperature is allowed to proceed for 1 hour,[8] after which the solution is treated with an excess of silver sulfate dissolved or suspended in hot water. The

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solution is allowed to cool and stand overnight at room temperature (or preferably in the icebox at as low a temperature as is practicable), and the insoluble guanidine-silver sulfate compound is separated by filtration.

The filtrate is neutralized with barium hydroxide to a pH of about 6.4 to 7.0, in two stages; the bulk of the barium sulfate is filtered off while the solution is decidedly acid, since the barium sulfate will be found to filter much more readily in acid than in neutral solution. The neutralization of the small remaining amount of acid is completed to a pH of 6.4 to 7.0, using bromthymol blue, a glass electrode, or some other convenient pH indicator. The solution is filtered through a Büchner funnel, using enough decolorizing carbon to prevent the clogging of the filter by the barium sulfate. The neutral filtrate is concentrated under reduced pressure at a low temperature to a thick sirup, which is taken up with about 500 ml of warm absolute alcohol. A small quantity of decolorizing carbon is added and the solution filtered. The filtered solution is evaporated again in vacuo to a thick sirup, which is diluted with a little warm absolute alcohol and seeded with *d*-ribose. Crystallization usually starts within a few minutes and is completed overnight. The crystals are collected on a filter, washed with alcohol, and dried.

Ribose may be purified by dissolving in a very small amount of water, adding alcohol, filtering through carbon, and allowing to stand until crystallization is complete, preferably in the icebox.

The mother liquors, both from the crude and from the recrystallized ribose, may be retreated to yield further crops of crystals.

Hydrolysis of adenosine picrate.—One hundred and fifty grams of recrystallized adenosine picrate is dissolved in 10 liters of boiling water. When solution is complete, 70 g of sulfuric acid is added and hydrolysis is allowed to proceed for 1 hour at 100° C. The solution is allowed to stand overnight at room temperature, or preferably in the refrigerator, in order that the insoluble adenine picrate may completely crystallize. After separation of the adenine picrate by filtration, the sulfuric acid in the filtrate is neutralized in two steps, as described for guanosine, and the filtrations in each case are made through a matt of decolorizing carbon on a large Büchner funnel. From this point on, the procedure is identical with that described above for guanosine.

The yield from 500 g of nucleic acid assaying 83 percent has been found to be about 35 g of ribose from the guanosine and 25 g from the adenosine picrate, or a total of 60 g of crystalline *d*-ribose.

NOTES

[1] Nucleic acid purchased from several chemical firms has been found satisfactory.

[2] If preferred, the nucleic acid may first be dissolved in water containing a little ammonia and the magnesia then added, although this procedure is not necessary.

[3] The sizes of vessels and the quantities of materials specified are based in part upon the capacity of the autoclave available. If the reaction is conducted in a flask, more vigorous stirring may be used without splashing.

[4] The yield is materially reduced if stirring is not used. This probably results from the formation of relatively insoluble magnesium nucleotides which, if not kept in suspension by stirring, cake upon the bottom and cause the hydrolysis to proceed less smoothly.

[5] At this stage the reaction of the filtrate should preferably be slightly alkaline, about pH 7.5 to 8.0. An acid reaction indicates that insufficient magnesia was used. It is important that the solution not be allowed to become acid during the hydrolysis, because at the high temperature employed there would be danger of hydrolyzing some of the riboside and so losing ribose in the reaction mixture.

[6] Avoid heating longer than is necessary as the guanosine is easily hydrolyzed. The same is true of adenosine.

[7] The decolorizing carbon should be thoroughly washed with hot water.

[8] To avoid bumping, a drying oven which will accomodate a 12-liter flask is excellent for carrying out the hydrolysis, both of guanosine and of adenosine picrate.

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21. *l*-SORBOSE

Biological source.—The biological synthesis of *l*-sorbose from *d*-sorbitol by bacterial fermentation has been developed by the Industrial Farm Products Research Division of the Bureau of Agricultural Chemistry and Engineering, and yields of more than 90 percent are obtained [1].

Crystallization.—Three parts of sorbose are dissolved with 2 parts of water containing a few drops of acetic acid. After the addition of a small quantity of a decolorizing carbon the hot solution is filtered. The clear filtrate is allowed to cool slowly while it is stirred. Crystallization takes place as the solution cools. After standing for several hours at room temperature or below, the crystals are separated and washed, first with a mixture of methyl alcohol (2 volumes) and water (1 volume) and then with undiluted methyl alcohol. About 50 percent of the crude sugar separates in the first crop of crystals. By evaporating the mother liquor in vacuo to a sirup of about 70 percent of total solids, additional sorbose crystallizes. In 11-percent aqueous solution, *l*-sorbose gives $[\alpha]_D^{20} = -43.7°$ initially, changing in several hours to $-43.4.°$

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22. *d*-TALOSE

Method.—[1, 2, 3] *d*-Talose may be prepared from galactose through the intermediate preparation of pentaacetylgalactose (see page 488), 1-bromoacetylgalactose (see page 500), triacetylgalactal (see page 532), and galactal. An aqueous solution of galactal (150 g in 1,500 ml of water) is cooled to 0°C and treated with a solution of 174 g of perbenzoic acid in 1 liter of ether.[1] The mixture is stirred at 0°C for 4 hours and for several additional hours while the temperature is allowed to rise slowly to room temperature. The aqueous phase is separated and extracted three times with ether and three times with chloroform. The purified aqueous solution is then concentrated in vacuo to a thin sirup (about 70 percent) and allowed to stand overnight. About 5 g of difficulty soluble monobenzoyltalose crystallizes and is separated by filtration and washed with water.[2]

The mother liquors are evaporated to a thin sirup which is taken up with methanol and allowed to crystallize. The crystals are separated and the mother liquor is again evaporated and crystallization allowed to take place. This process is repeated until no further crystallization occurs.[3] The various crops are then combined and

extracted for an hour with eight times their weight of gently boiling methanol. The undissolved material[4] is removed by filtration and the filtrate is evaporated to a thin sirup which crystallizes to give crude *d*-talose.[5] The sugar is recrystallized by dissolving it in water and concentrating the solution to a sirup which is diluted with methyl alcohol and seeded. Pure *d*-talose may be obtained by recrystallizing once more the material obtained. From 150 g of galactal a total of about 50 g of *d*-talose may be obtained. This corresponds to a yield of about 80 g of *d*-talose from 500 g of galactose.

The form of *d*-talose obtained under ordinary conditions melts at 133° to 134°C and in 4-percent aqueous solution exhibits a rapid complex mutarotation from an initial value of $[\alpha]_D^{20}=+68.0°$ to an equilibrium value of $[\alpha]_D^{20}=+20.8°$.

The pyridine rearrangement of galactonic acid and the reduction of the talonic acid formed has also been used for the preparation of talose [4, 5].

NOTES

[1] *Preparation of perbenzoic acid.*—Thirty grams of finely ground sodium peroxide is added with vigorous stirring to 400 ml of ice and water and after the addition of 200 ml of cold ethyl alcohol (−5°C), 25 ml of benzoyl chloride dissolved in 100 ml of cold ether is added. The mixture is stirred for several minutes and is then filtered through a large Büchner funnel. The filtrate, after acidification with 700 ml of cold (0°C) normal sulfuric acid, is extracted with four 150-ml portions of ether. The solution should be kept as cold as possible until the final acidification; about 20 g of perbenzoic acid is obtained.

[2] Alcohol should not be used for washing this product.

[3] Additional material may be obtained from the mother liquor by heating it near the boiling point with 0.05 *N* sulfuric acid for several hours. The cold solution is extracted with ether, neutralized with barium carbonate, filtered, and evaporated as before. This treatment hydrolyzes the benzoyl derivatives of galactose and talose which may be present.

[4] Usually this material is nearly pure galactose with an optical rotation between $[\alpha]_D^{20}=+76°$ and $+80°$. If the rotation is below this, another extraction is advantageous.

[5] The optical rotation of this material is between $[\alpha]_D^{20}=+25°$ and $+30°$.

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23. TURANOSE (3-(α-*d*-GLUCOPYRANOSIDO)-*d*-FRUCTOSE)[1]

Method.—[1, 2, 3] One hundred grams of pure melezitose[2] is dissolved in 1 liter of boiling water containing 4 ml of concentrated sulfuric acid. The solution is boiled gently for 15 minutes and is then neutralized with an excess (10 g) of calcium carbonate and cooled to 37° C. A cake of compressed baker's yeast and 20 ml of nutrient solution[3] are added, and fermentation is allowed to take place at 37° C for about 4 days, after which about 10 g of a decolorizing carbon is added and the solution is filtered. The filtrate is evaporated in vacuo to a sirup of about 88 percent of total solids ($n_D^{20}=1.511$). The sirup is taken up with 150 ml of methyl alcohol, and after the addition of 5 g of a decolorizing carbon the solution is filtered. The filtrate is seeded with crystals of turanose[4] and allowed to stand. After several days the crystals are separated and the mother liquor is concentrated again

to give additional product. The total yield from 100 g of melezitose is about 50 g.

Recrystallization.—One hundred grams of turanose is dissolved in 100 ml of hot water. After adding 5 g of a decolorizing carbon, the solution is filtered and then evaporated in vacuo to a sirup ($n_D^{20}=1.490$) containing about 80 percent of total solids. This sirup is dissolved in 100 ml of hot methyl alcohol. After the addition of 5 g of a decolorizing carbon, the hot solution is filtered. The filtrate, after cooling to room temperature, is seeded and preferably stirred while crystallization takes place. After several hours the crystals are collected on a filter and washed with methyl alcohol. The yield is about 75 g. The remaining sugar is reclaimed by concentrating the mother liquor, adding methyl alcohol, and separating the crystals which form.

In 4-percent aqueous solution, turanose gives $[\alpha]_D^{20}=+27.3°$ initially, changing in the course of an hour to an equilibrium value of $+75.8°$.

NOTES

[1] The 3-glucosidofructose structure for turanose was first proposed by Isbell and Pigman [4].

[2] The method for obtaining melezitose is described on page 472.

[3] The nutrient solution is prepared by dissolving 2.5 g of NH_4NO_3, 0.3 g of KH_2PO_4, and 0.25 g of $MgSO_4.7H_2O$ in 100 ml of water.

[4] The seed crystals originally used at this Bureau were part of the product first discovered by D. H. Brauns.

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24. *d*-XYLOSE

Method.[1]—[1] One kilogram of shredded or broken corn cobs is boiled [2] for 3 hours with 6 liters of 7-percent sulfuric acid, after which the insoluble residue is separated on a filter and washed with water. The aqueous solution is neutralized with calcium carbonate, and after removal of the insoluble calcium sulfate, the liquor is treated with baker's yeast. When the ensuing fermentation is complete, about 100 g of decolorizing carbon is added and the solution is filtered.[3] The filtrate is concentrated in vacuo to a sirup ($n_D^{20}=1.442$, 60 percent of total solids), which is then diluted with 3 volumes of methyl alcohol. After separation of the resulting precipitate, the alcoholic solution is evaporated in vacuo to a sirup (85 percent of total solids, $n_D^{20}=1.503$), which is mixed with 250 ml of methyl alcohol and seeded with crystalline *d*-xylose. After standing for several days, the crystalline product is separated and washed with 75 percent by volume of aqueous methyl alcohol. The yield is about 12 percent.[4]

Recrystallization.—One kilogram of xylose is dissolved with 400 ml of water containing a few drops of acetic acid. After the addition of 15 g of a decolorizing carbon, the hot solution is filtered and the filtrate is cooled and kept in gentle motion for several hours while crystallization takes place. The crystals which form are separated and washed with water or with aqueous alcohol. The yield is about 50 percent in the first crop. The sugar in the mother liquor crystallizes readily from sirups of about 75 percent of total solids.

α-*d*-Xylose melts at 145° C and in 4-percent solution gives $[\alpha]_D^{20}=+93.6°$ initially, changing in several hours to +18.8°.

NOTES

[1] The commercial production of xylose from cottonseed hulls is described by Schreiber, Geib, Wingfield, and Acree [2].

[2] The hydrolysis can be conducted in an Inchronel metal pot.

[3] In the event that the solution at this point is dark colored, it should be clarified further by treatment with basic lead acetate followed by hydrogen sulfide [3].

[4] By using the basic lead acetate clarification mentioned in note 3, the method can be used for the preparation of xylose from cottonseed hulls.

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XXXI. METHODS FOR THE PREPARATION OF CERTAIN SUGAR DERIVATIVES

In this chapter characteristic methods for the production of acetal and ketal derivatives, esters, ethers, glycosides, mercaptals, and oxidation and reduction products are given. A résumé of the characteristic properties of each group is followed by typical directions for the synthesis of specific compounds and a list of pertinent references. The methods are selected from those found in the literature as being of general use. No attempt has been made to give a complete bibliography or to report original work. Many of the original methods have been modified and improved in various ways. The physical constants of the products are selected from data in the literature and are not always to be found in the articles describing the method. Additional literature references are cited in the table of sugar derivatives (p. 704). Whenever possible the examples were chosen from the work of the members of this Bureau's staff. For this reason a general method applicable to any sugar may have been illustrated by a specific example for a rare and relatively inaccessible sugar.

1. ACETAL AND KETAL DERIVATIVES

General characteristics of the acetal and ketal derivatives.—The sugars and many of their derivatives condense with aldehydes and ketones to give compounds which are useful for the preparation of partially substituted sugars, and for the preparation and purification of derivatives and products of diverse types.

The configurational relationships of the hydroxyls determine in large measure whether or not a condensation will take place. The effect of configuration in relation to the particular ketone or aldehyde used has been reviewed [1, 2].

The condensation of acetone with a sugar is carried out by mixing the sugar with acetone and a dehydrating agent. Some of the dehydrating agents which have been used are hydrogen chloride [3], anhydrous copper sulfate [4], sulfuric acid [5, 6], zinc chloride [7], and phosphorus pentoxide [8]. The use of anhydrous copper sulfate rather than an acid is often desirable when glycosides are condensed

with acetone, as otherwise ring shifts and other structural changes may occur. Most sugars give diacetone derivatives. The monoacetone sugars are most easily prepared from the diacetone derivatives by carefully regulated acid hydrolysis. Usually the acetone groups are split off at different rates; for example, the acetone group in the 5,6 position of 1,2-5,6-diacetone-*d*-glucose is hydrolyzed 40 times as fast as that in the 1,2 position.

Examples of the condensation of sugars with aldehydes are the benzylidine sugars, which are prepared by the action of benzaldehyde on the sugars in the presence of a dehydrating agent, such as phosphorus pentoxide [9], anhydrous sodium sulfate [9], zinc chloride [10], or hydrogen chloride [11]. The benzylidine groups are removed by treatment with acid in water solution or by hydrogenation with a palladium catalyst in alcoholic solution [12]. The di-*o*-nitrobenzylidine derivatives of a number of sugars have been prepared and are interesting in that they resist acylation, and isomerize to *o*-nitrosobenzoates in the presence of light, sometimes with a simultaneous Walden inversion [13]. The preparation of 4,6-benzylidine-α-*d*-glucose is described later in this section. Condensation products of sugars and derivatives with acetaldehyde (ethylidine sugars) [14,15], furfuraldehyde [16], and formaldehyde [17] have also been prepared.

(a) SULFURIC ACID METHOD FOR THE PREPARATION OF ACETONE DERIVATIVES

(1) 1,2-5,6-Diacetone-*d*-glucose.

Method [6].—One hundred grams of anhydrous dextrose is shaken with 2 liters of dry acetone containing 80 ml of concentrated sulfuric acid. After 5 hours, when most of the sugar has dissolved, an excess of anhydrous sodium carbonate is added, the solution is filtered, and the filtrate is evaporated to a heavy sirup which is taken up with cold water. A small amount of amorphous material which separates is discarded. The solution is extracted three times with benzene and the extracts are washed with water. The combined aqueous solution and washings of the benzene extracts are treated with a decolorizing carbon and are then extracted a number of times with one-fifth of their volume of chloroform. The chloroform extract, upon drying and evaporation in vacuo, yields 102 to 106 g of crystalline diacetoneglucose. The mother liquor, after concentration in vacuo to a heavy sirup which is taken up with alcohol, gives about 20 g of monoacetoneglucose.

The pure 1,2-5,6-diacetone-*d*-glucose melts at 110° to 111° C and gives $[\alpha]_D^{20}=-18.5°$ (water, $c=5$). The 1,2-monoacetone-*d*-glucose melts at 161° C and gives $[\alpha]_D^{20}=-11.8°$ (water, $c=8$).

(2) 1,2-4,5-Diacetone-*d*-fructose.

Method [4].—Seventy-five grams of dry powdered levulose is shaken with 1½ liters of acetone and 7½ ml of sulfuric acid for 20 hours. The reaction product is neutralized with ammonia gas, filtered, and concentrated in vacuo. The partially crystallized sirup is extracted with ether. The undissolved sirup is mainly 2,3-monoacetonefructose which can be extracted by shaking with 100 ml of 5 *N* sodium hydroxide. The ether solution containing 1,2-4,5-diacetonefructose is purified by washing, first with dilute (1:10) sulfuric acid and then with dilute sodium hydroxide solution. The ether solution, dried with sodium sulfate, is evaporated in vacuo and the residue recrystallized from

petroleum ether. The yield is 32 g of pure 1,2-4,5-diacetone-*d*-fructose, which has a melting point of 118° to 119° C and gives $[\alpha]_D^{20} = -146.6°$ (chloroform, $c=2.5$) [18].

(b) COPPER SULFATE METHOD FOR THE PREPARATION OF ACETONE DERIVATIVES

(1) MONOACETONE AND DIACETONE DERIVATIVES OF METHYL α-*d*-MANNOPYRANOSIDE.

Method [19].—Ten grams of methyl α-*d*-mannopyranoside is shaken at room temperature with 400 ml of dry acetone for 10 days in the presence of anhydrous copper sulfate.[1] The filtered solution is concentrated in vacuo to a sirup from which some unchanged methyl α-*d*-mannoside is eliminated by taking up the sirup in cold acetone. The resulting sirup is separated into two fractions by a vacuum distillation at 0.03 mm pressure.

One fraction (1.6 g), which distills at a bath temperature of 125° to 130° C, crystallizes slowly when kept in a desiccator. This product, methyl 2, 3-4, 6-diacetone-α-*d*-mannoside, after recrystallization from aqueous alcohol, melts at 76° to 77° C and gives $[\alpha]_D^{20} = +3°$ (methyl alcohol, $c=2.4$). A second portion (0.8 g) distills at a bath temperature of 165° to 170° C and crystallizes when seed of methyl 2,3-monoacetone-α-*d*-mannopyranoside is added. This substance melts at 105° C and gives $[\alpha]_D^{20} = +24.3°$ (water, $c=4$). [20]

NOTES

[1] In order to prevent ring changes during the reaction, it is necessary that the acetone be free of methyl alcohol. Better yields may be obtained by carrying out the reaction at 50° C. Certain glycosides, such as methyl β-*d*-mannoside, require a longer reaction time, in some cases several months.

(c) HYDROLYSIS OF THE DIACETONE DERIVATIVE TO GIVE A MONOACETONE DERIVATIVE

(1) 1,2-MONOACETONE-*d*-GLUCOSE.

Method [21].—Fifty grams of 1,2-5,6-diacetone-*d*-glucose (see p. 483) is dissolved in 400 ml of ethyl acetate containing 4 ml of concentrated nitric acid. The solution is heated to boiling and cooled. The 1,2-monoacetone-*d*-glucose which separates at once is purified by recrystallization from water or neutral ethyl acetate.

(d) ZINC CHLORIDE METHOD FOR PREPARING BENZYLIDINE DERIVATIVES

(1) 4,6-BENZYLIDINE-α-*d*-GLUCOSE.

Method [12].—One hundred and thirty grams of anhydrous dextrose and 100 g of finely powdered fused zinc chloride are shaken with 300 ml of freshly distilled benzaldehyde for 24 hours on the shaking machine. The thick liquid is then mixed with 400 ml of ice-cold water, whereupon crystallization takes place. The mixture is filtered and the crystals are washed, first with cold water and then with petroleum ether. Between 60 and 70 g of material is obtained. The crystals are recrystallized several times from 10 times their weight of hot water to which enough ammonia is added to make the solution alkaline. About 20 to 25 g of pure material is obtained which melts at 188° C. 4,6-Benzylidine-α-*d*-glucose is dextrorotatory in methyl alcoholic solution and mutarotates to a value of about −4°.

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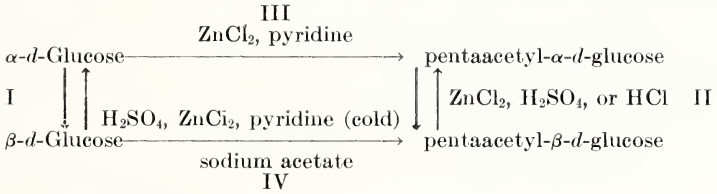
2. ACETYL DERIVATIVES

General characteristics of the acetylation reactions.—The acetylation of the nonreducing sugars and other derivatives which consist of a single modification can be carried out by almost any method which does not affect the rest of the molecule, but the acetylation of the reducing sugars is complicated by the existence of several ring modifications. For this reason it is necessary to select a method which will give the desired crystalline product. The isomer obtained depends upon the catalyst used in the acetylation and upon the temperature. The following general scheme [1] illustrates the effect of these factors on the acetylation of glucose. At low temperatures (0° C) the equilibria represented by reactions I and II are only slowly



established and the acetylation reactions III or IV take place without isomerization. By using pyridine (or zinc chloride) and a low temperature, the alpha aldohexose yields the alpha pentaacetate and the beta aldohexose yields the beta pentaacetate. At higher temperatures, in the presence of acid catalysts, isomerization between the acetates takes place and the products obtained depend upon the position of the equilibrium represented by the reaction II. For glucose the equilibrium mixture of pentaacetates consists of 90 percent of the alpha and 10 percent of the beta pentaacetylglucose [2]. For most sugars the alpha acetate predominates in the equilibrium mixture

and consequently the use of acid catalysts, such as zinc chloride, and a relatively high temperature (20° to 110° C) gives the alpha acetate from either the alpha or beta sugar. With sodium acetate as a catalyst at a high temperature, the equilibrium between the alpha and beta sugars is established, while the equilibrium between the acetates is not. Since the beta sugar is acetylated more rapidly than the alpha, the principal product is then the beta acetyl sugar. The diagram also illustrates how the alpha acetates may be prepared from the beta acetates. A mixture of sulfuric acid, acetic acid, and acetic anhydride has been found to be a very useful isomerization reagent [3]. In some cases the equilibrium solutions contain appreciable quantities of the furanose modification, and both pyranose and furanose modifications are produced. The four cyclic acetates of galactose [4,5] have been separated.

Sugar acetates with the acetyl groups of carbons 1 and 2 in the *trans* position may be prepared by treating the halogeno-acetyl sugars with silver acetate. The replacement of the halogen in the halogeno-acetyl sugars is usually accompanied by Walden inversion, and as pointed out by Isbell [6], the course of the reaction depends on the *cis-trans* relationship of the halogen and the adjacent acetyl group. If the halogen and the adjacent acetyl group are on the same side of the sugar ring (*cis*), the halogen may be replaced with Walden inversion with the formation of a normal acetate, glycoside, or other sugar derivative. But if the halogen and the adjacent acetyl group are on opposite sides of the sugar ring (*trans*), the acetyl group undergoes an intramolecular reaction and forms an orthoacetic ester.

The first ketose, for which several acetyl derivatives, halogeno-acetyl derivatives, and ketosides were obtained in the crystalline state, is fructose. For obtaining these derivatives of fructose, it was found [7, 8, 9] that acetylation at low temperature leads to crystalline derivatives. This observation holds also for sorbose and may be valuable if crystalline derivatives of other ketoses are desired. Tetra-acetyl-*d*-fructose [7, 8] is an important intermediate for the preparation of other derivatives of fructose. Several acetates of turanose and sorbose have been described [10, 11].

The partially acetylated sugar derivatives may be considered in two classes: (1) Those with free reducing groups, and (2) those with free hydroxyl groups. The first class may be subdivided further into open-chain, pyranose and furanose derivatives. The open-chain derivatives are usually prepared from the acetylated mercaptals by removing the mercaptal groups by treatment with cadmium carbonate in the presence of mercuric chloride. A few open-chain derivatives have been obtained by direct acetylation. The partially acetylated furanoses and pyranoses are prepared from the halogen acetates by treatment with moist silver oxide, or from the orthoacetates by reaction with aqueous acid. The partially acetylated derivatives containing free hydroxyl groups are prepared frequently from substances which contain easily removable groups such as triphenylmethyl, benzyl, *p*-toluenesulfonyl, ethylidene, and benzilidene groups.

(a) LOW-TEMPERATURE PYRIDINE METHOD OF ACETYLATION [12, 13]

Acetylation of the sugars with acetic anhydride and pyridine at a low temperature generally yields acetylated products which have the

same structure as the original sugar, and therefore this reaction is of first importance for studying the structure of the sugars. Since the product usually consists of a single isomer, the method yields products that crystallize readily.

(1) PENTAACETYL-α-*d*-TALOSE.

Method [14].—Five grams of powdered α-*d*-talose is added to a cold mixture (0° C) of 35 ml of pyridine and 23 ml of acetic anhydride. The mixture is shaken at 0° C for several days (until the sugar dissolves) and is then poured into 125 ml of ice and water, with stirring. In a short time pentaacetyl-α-*d*-talose crystallizes and the crystals are separated by filtration.[1] The filtrate is extracted with chloroform or benzene and the extract is washed, first with sodium bicarbonate solution, then four times with dilute copper sulfate solution, and finally with water. The chloroform solution is evaporated in vacuo to a sirup, which is dissolved in ethyl alcohol and allowed to crystallize. The product is separated, combined with the first crop of crystals, and recrystallized from hot ethyl alcohol. The total yield is about 8 g. Pentaacetyl-α-*d*-talose melts at 106° to 107° C and gives $[\alpha]_D^{20}=+70.2°$ (chloroform, $c=4$).

NOTES

[1] Acetylated sugars which do not crystallize at this point are extracted with chloroform. The chloroform solution is washed, as described for the filtrate, and evaporated to a sirup, which is taken up in petroleum ether or other suitable solvent. In working up new products the best solvent to use can be determined by experimentation. Frequently crystallization is inhibited by the presence of pyridine, acetic anhydride, or chloroform. These can be eliminated by careful washing, evaporation, or by fractional extraction of the residue with suitable solvents.

(b) LOW-TEMPERATURE SULFURIC ACID METHOD OF ACETYLATION [15]

In some cases low-temperature acetylation with sulfuric acid as a catalyst has given crystalline products when other methods were not successful. This method can be used for either aldoses or ketoses.

(1) PENTAACETYL-β-*d*-FRUCTOSE.

Method [9].—Forty grams of finely powdered levulose is added to a cold mixture of 240 ml of acetic anhydride and 10 ml of concentrated sulfuric acid. The mixture is kept in an ice-salt bath and stirred until all the sugar goes into solution, after which the solution is shaken with about 500 ml of ice water, neutralized with sodium bicarbonate, and separated from the excess of solid bicarbonate by filtration. The residue on the filter is washed with chloroform to dissolve any acetylated sugar, and the filtrate is extracted with chloroform for the same purpose. The chloroform solutions are mixed, dried with calcium chloride, and distilled in vacuo to a small volume (30 to 50 ml). This solution is then spread in a thin layer over a flat crystallizing dish and a strong current of air is passed over the yellowish fluid until the odor of chloroform disappears and that of acetic anhydride becomes noticeable. The sirup is then placed in a vacuum desiccator, near potassium hydroxide and on scratching the dish at intervals, the sirup soon crystallizes to a solid mass. This is stirred in a mortar with some ether and filtered. About 16 g (or 20 percent of the theoretical) of pure pentaacetyl-β-*d*-fructose is obtained. The substance is easily recrystallized from ether, and by slow evaporation the solution yields brilliant, clear crystals which melt at 108° to 109° C and give $[\alpha]_D^{20}=-120.9°$ (chloroform, $c=5$).

(c) LOW-TEMPERATURE ZINC CHLORIDE METHOD OF ACETYLATION

By variation of the conditions used in the acetylation, with zinc chloride as a catalyst, it is sometimes possible to prepare acetyl derivatives of different structure. Acetylation of levulose at 0° C gives a tetraacetylfructopyranose.[1] By continuing the acetylation at a higher temperature the open-chain pentaacetylfructose is obtained.

NOTE

[1] The preparation of 1,3,4,5-tetraacetyl-*d*-fructose is given on page 492.

(1) PENTAACETYL-β-*d*-MANNOSE.

Method [16].—Four grams of fused zinc chloride is dissolved in 40 g of acetic anhydride, the solution is cooled to 0° C, and 10 g of powdered β-*d*-mannose is added in small portions with shaking while the mixture is kept at 0° C. When all of the sugar is in solution (24 hours), the mixture is poured into ice water and stirred until the insoluble residue crystallizes. Then the product is separated by filtration and recrystallized from alcohol. Pentaacetyl-β-*d*-mannose melts at 117° to 118° C and gives $[\alpha]_D^{20}=-25.2°$ (chloroform, $c=3$).

(d) SODIUM ACETATE METHOD OF ACETYLATION

This is one of the most satisfactory methods for preparing acetyl sugars, because the catalyst is easily removed by washing with water. The method can be used for small or large quantities of material.

(1) PENTAACETYL-β-*d*-GALACTOSE.

Method [17].—Twenty-seven hundred milliliters of acetic anhydride (technical 90 to 95 percent) is heated to about 100° C and 220 g of anhydrous sodium acetate [1] is added. In small portions, 500 g of *d*-galactose is added with stirring in the course of an hour, [2] and when the addition is completed, the solution is heated at about 100° C for about 1 hour. The solution is cooled to room temperature, poured into 8 liters of ice water, and stirred for several hours. The acetylated product is then extracted with a total of 6 liters of benzene (technical) or with chloroform.[3] The extracts are washed with water, dried, and concentrated under reduced pressure to a thick sirup, which is allowed to crystallize. The crystals are separated by filtration and washed with mixtures of benzene and petroleum ether. The crude material is recrystallized by dissolving it in the minimum amount of boiling ethyl alcohol, adding a decolorizing carbon, filtering while hot, and allowing the solution to cool. The yield of recrystallized material is 550 g, and about 75 g more can be obtained from the original mother liquors and from those remaining after the recrystallization.

Pentaacetyl-β-*d*-galactose has a melting point of 142° C and an optical rotation, $[\alpha]_D^{20}=+25°$ (in chloroform). From the mother liquors other isomeric acetates may be obtained [4,5].

NOTES

[1] Anhydrous sodium acetate is prepared by heating the hydrate in a stainless-steel container until the product has melted, solidified, and finally melted again. The hot liquid is poured in a thin layer over a slab of stone and the product is ground in a mortar and bottled. The slight charring which occurs by this method can be avoided by drying the acetate *in vacuo* at a lower temperature.

[2] The sugar must be added slowly; otherwise the reaction may suddenly become too vigorous.

[3] With many sugars the acetylated product crystallizes from solution, in which case the extraction may be omitted and the crude product is separated by filtration, and recrystallized from alcohol.

(e) HIGH-TEMPERATURE ZINC CHLORIDE METHOD OF ACETYLATION [18]

Acetylation with hot acetic anhydride and zinc chloride usually gives the alpha isomer. The zinc chloride is dissolved in hot acetic anhydride and the sugar is added in small portions. After the reaction is complete the mixture is cooled and then poured into ice water. The acetylated sugar is separated by extraction or by filtration. The high-temperature zinc chloride acetylation can be used for converting glycosides and fluoro-acetyl derivatives to the fully acetylated sugars.

(1) Octaacetyl-4-(β-*d*-glucosido)-α-*d*-mannose.

Method [19].—A solution of 30 g of fluoro-heptaacetyl-4-glucosido-mannose and 2 g of fused zinc chloride in 150 ml of acetic anhydride is heated on the steam bath for 30 minutes and is then poured into a large amount of ice water. After the mixture is stirred for several hours, the crystallized product is separated by filtration and washed with methyl alcohol. About 22.5 g of octaacetyl-4-(β-*d*-glucosido)-α-*d*-mannose is obtained. After recrystallization from methyl alcohol the pure material melts at 202° to 203° C and gives $[\alpha]_D^{20}=+36.2°$ (chloroform, $c=2$).

(f) PREPARATION OF ACETYL DERIVATIVES FROM HALOGENO-ACETYL DERIVATIVES

(1) Tetraacetyl-β-*d*-xylose.

Method [20].—Four grams of bromo-triacetylxylose [1] is dissolved in 75 ml of glacial acetic acid and the solution is shaken for a few minutes [2] with 5 g of silver acetate. A small amount of a decolorizing carbon is added, the solution is filtered, diluted with water, and extracted with chloroform. The chloroform extract is washed with water and is then evaporated under reduced pressure to a thick sirup, which is dissolved in ether and allowed to crystallize. The pure tetraacetyl-β-*d*-xylose [3] has a melting point of 128° C and gives $[\alpha]_D^{20}=-24.7°$ (chloroform, $c=5$) [21].

The procedure described may also be used with chloroacetyl derivatives, but the reaction is carried out at a temperature of 50° to 60° C.

NOTES

[1] This compound may be made according to the procedure described for bromo-tetraacetylglucose on page 500.

[2] A small portion of the solution after filtration should give a negative Beilstein copper-wire test for halogen.

[3] For some sugars quantities of the alpha isomer are also produced.

(g) INTERCONVERSION OF ACETATES

(1) Preparation of Pentaacetyl-α-*d*-mannose from Pentaacetyl-β-*d*-mannose.

Method [16].—Twenty grams of the pentaacetyl-β-*d*-mannose is dissolved in 30 ml of acetic anhydride containing 1 g of fused zinc chloride, and the solution is heated on the steam bath until no further change in the rotation is observed (about 30 minutes). The solution is cooled, mixed with 500 ml of ice water, and the acid neutralized with sodium bicarbonate. A thick gummy substance separates and

is removed, washed in cold water, and dissolved in boiling water. Upon cooling, the solution deposits about 7 g of the crystalline pentaacetyl-*α*-*d*-mannose, which is further purified by recrystallization from hot water. The purified material melts at 64° C and gives $[\alpha]_D^{20}=+55.0°$ (chloroform, $c=4$).

(2) Preparation of Hexaacetyl-*α*-*d*-*α*-mannoheptose from Hexaacetyl-*β*-*d*-*α*-mannoheptose.—Alpha acetates can be prepared from beta acetates by treatment with sulfuric acid in a mixture of acetic anhydride and acetic acid. The isomerizing reagent is prepared by adding dropwise 4.6 ml of concentrated sulfuric acid to a mixture of 140 ml of acetic anhydride (95 percent) and 60 ml of glacial acetic acid cooled in a bath of ice and salt.

Method [3].—A solution of 5 g of hexaacetyl-*β*-*d*-*α*-mannoheptose in 25 ml of the isomerizing reagent is prepared and allowed to stand at 20° C for 24 hours. The mixture is then poured into ice water, and the product which separates is washed with sodium bicarbonate solution and again with water. The acetate is then dissolved in ether and after the addition of petroleum ether to saturation, hexaacetyl-*α*-*d*-*α*-mannoheptose crystallizes. The yield obtained by Montgomery and Hudson was 3.8 g. The purified product melts at 75° to 76° C and gives $[\alpha]_D^{20}=+120.8°$ (chloroform, $c=1$).

Essentially the same method can be used for transforming other acetylated pyranosides [22]. Acetylated furanosides frequently give open-chain acetates.

(h) PREPARATION OF OPEN-CHAIN ACETATES

In a few cases, particularly with the ketoses, open-chain acetyl derivatives may be prepared by direct acetylation of the sugar (see p. 491). In general, however, they are obtained by the acetylation of open-chain derivatives, such as the mercaptals [23] and oximes [24], and the subsequent regeneration of the carbonyl group by removal of the substituent group. The mercaptals have been most commonly used as the starting materials. However, in cases where the mercaptals are unknown or when the conditions for their formation are too severe (as for disaccharides), the oximes and semicarbazones are preferable. The benzoyl-aldehydo sugars have also been prepared.

(1) Pentaacetyl-*aldehydo*-*d*-glucose.

Method [23].—Five grams of glucose ethyl mercaptal (prepared as described for galactose on p. 521) is acetylated by the pyridine method described on page 486. The sirup resulting from the acetylation crystallizes after standing for a week or two in the ice box. The crystalline material, separated by one filtration and washed with cold water, weighs about 8 g. The material is recrystallized from aqueous methyl alcohol to give pure pentaacetylglucose ethyl mercaptal which melts at 45° to 47°C.

A solution of 90 ml of acetone and 45 ml of water is placed in a three-necked round-bottomed flask provided with a reflux condenser and a mercury-sealed mechanical stirrer. Pentaacetylglucose ethyl mercaptal (25.2 g) is then dissolved in the solution, and an excess of washed cadmium carbonate (45 to 50 g) is added. A solution of 49.5 g of mercuric chloride in 72 ml of acetone is then gradually added to the rapidly stirred mixture and the stirring continued at room temper-

ature for 24 hours, during which time small amounts of cadmium carbonate are added. After this period the rapidly stirred solution is heated in a water bath to 50°C and held at this temperature for 15 minutes. The temperature is then raised and the solution, after being refluxed gently for 15 minutes, is filtered into a flask containing cadmium carbonate. The precipitate (EtS-Hg-Cl) is washed with acetone. The filtrate containing an excess of cadmium carbonate is concentrated in vacuo at 30° to 35°C to a thick sirup from which water is removed by repeated addition of acetone, and distillation. The final residue is extracted with warm chloroform and the chloroform evaporated in a vacuum desiccator. The crude product which crystallizes is separated and dissolved in 50 ml of hot acetone. Alcohol-free ether (25 ml) is added to the solution and then petroleum ether to saturation. After several hours at 0°C the crystalline material is separated, washed with an ether-acetone solution and dried. About 10 g of material is obtained from the first crystallization and about 2 g more may be obtained by adding petroleum ether to the mother liquors. The pure pentaacetyl-aldehydo-*d*-glucose has a melting point of 116° to 118°C and gives $[\alpha]_D^{24} = -4.8°$ (chloroform, $c=5$).

(2) Pentaacetyl-*keto*-*d*-fructose

Method [8, 25].—Ten grams of finely powdered levulose is added in one portion to a solution of 1 g of fused zinc chloride in 100 ml of acetic anhydride cooled in an ice bath. The mixture is stirred vigorously at 0°C for 4 hours, during which time most of the sugar dissolves. The temperature is then kept at 20° to 25°C for 1 hour and finally at 50°C for 2 hours. The cooled solution is stirred with an equal volume of ice water for 1½ hours and is then further diluted and neutralized with an excess of sodium bicarbonate. The chloroform solution of the gummy precipitate, united with the chloroform extracts of the water solution, is dried with calcium chloride, filtered, and evaporated in vacuo to a sirup which is dissolved in about 50 ml of absolute ether. This solution on standing overnight in the ice box deposits about 10 g of crude crystalline pentaacetyl-*keto*-*d*-fructose.

The pure pentaacetyl-*keto*-*d*-fructose melts at 70°C and gives $[\alpha]_D^{20} = +34.7°$ (chloroform, $c=8$).

(i) PREPARATION OF PARTIALLY ACETYLATED PYRANOSES

Acetates containing free reducing groups are prepared by treating the halogeno-acetyl sugars with moist silver oxide or carbonate. They can be prepared also by the hydrolysis of orthoesters and occasionally by partial acetylation.

(1) Heptaacetyl-4-(β-*d*-glucosido)-*d*-mannose

Method [26].—Two grams of bromo-heptaacetyl-*d*-glucosidomannose is added to 50 ml of cold acetone containing 5 ml of water and 5 g of silver carbonate. The mixture is shaken until all the bromine is converted into silver bromide, which is separated by filtration. The solution is allowed to evaporate spontaneously in an open beaker. Slender, prismatic, needlelike crystals separate during the course of several hours. The crystals are collected upon a filter and washed with water. The yield is about 1½ g. After recrystallization from hot water, in which they are difficultly soluble, the crystals melt at 110°C and give $[\alpha]_D^{20} = +11.7°$ (chloroform, $c=5$).

(2) Hexaacetyl-4-(β-*d*-glucosido)-*d*-mannose.

Method [26].—A 5-g sample of 1, 2-(hexaacetyl-4-glucosido-mannose) methyl orthoacetate is suspended in 50 ml of cold absolute methyl alcohol, and 4 ml of methyl alcohol containing 0.34 g of dry hydrogen chloride is added. The flask is shaken until solution is complete (about 1 minute) and then allowed to stand at room temperature. After 10 minutes the acid solution is mixed with a paste consisting of 10 g of silver carbonate and 2 ml of water. The mixture is stirred until a negative test for halogen is obtained; then the silver salts are removed by filtration, and the solution is evaporated in vacuo to a thick sirup from which hexaacetyl-4-glucosidomannose crystallizes in rectangular prisms. It is difficulty soluble in water, fairly soluble in ether, and very soluble in chloroform. The crude product (3.8 g) is recrystallized from hot ethyl alcohol.

Hexaacetyl-4-(β-*d*-glucosido)-*d*-mannose melts at 171°C and gives $[\alpha]_D^{20}=+21.7°$ (chloroform, $c=2$).

(3) 1,3,4,5-Tetraacetyl-*d*-fructose.

Method [8, 27].—Sixty-six grams of freshly powdered levulose is added to a solution of 6 g of anhydrous zinc chloride in 340 ml of acetic anhydride which is cooled by an ice-and-salt mixture. During 16 hours of stirring at 0° C the fructose gradually disappears and small needles crystallize from the solution.[1] Then the mixture is stirred at −15° C for 1 hour and filtered. The unwashed crystals are transferred to a desiccator and dried over sodium hydroxide in vacuo until free from acetic anhydride. About 47 g of crude tetraacetylfructose is obtained. On neutralizing the mother liquor with solid sodium bicarbonate, a half-solid, sticky mass separates. This is dissolved in chloroform, the solution is washed three times with water, dried with calcium chloride, and concentrated under reduced pressure to a thin sirup. The sirup is dissolved in ether, poured into a crystallizing dish, and allowed to crystallize in a desiccator. About 13 g of the tetraacetate is obtained. The combined crops are dissolved in chloroform, and the solution, after filtering, is concentrated in vacuo to a thin sirup. Upon addition of ether, and cooling, the substance crystallizes in about 45-percent yield. Pure 1,3,4,5-tetraacetyl-*d*-fructose melts at 131° to 132° C and gives $[\alpha]_D^{20}=-91.6°$ (chloroform, $c=3$).

NOTE

[1] If the temperature is allowed to rise, pentaacetyl-*keto*-fructose is formed [25] (see p. 491).

(j) PREPARATION OF ORTHOACETATES

(1) 1,2-(Hexaacetyl-4-glucosidomannose) Methyl Orthoacetate and Methyl Heptaacetyl-4-(β-*d*-glucosido)-β-*d*-mannopyranoside.

Method[1] [26].—Twenty-five grams of bromo-heptaacetyl-4-glucosidomannose is mixed at 0° C[2] with 25 g of dry freshly prepared silver carbonate[3] in 250 ml of anhydrous methyl alcohol. After being shaken for 30 minutes, the solution is filtered. The filtrate, which should give a negative Beilstein copper-wire test for halogen, is concentrated in vacuo to a thick sirup, which is taken up with ether and allowed to crystallize. The evaporated mother liquor when taken up with alcohol deposits additional small crops of crystals. About 17 g of crystalline material is obtained, which consists of the hexagonal or diamond plates of 1,2-(hexaacetyl-4-glucosidomannose) methyl ortho-

acetate mixed with a small amount of the acetylated glycoside.[2] The crystals are fractionally recrystallized from absolute ethyl alcohol[4] and 14 g of the pure orthoacetate derivative is obtained. It melts at 167° C and gives $[\alpha]_D^{20}=-13°$ (chloroform, $c=3$). The material left after the separation of the orthoacetate consists of the acetylated beta glycoside and some of the orthoacetate. This mixture is separated by fractional crystallization, first from water and then from absolute alcohol. In these solvents the acetylated beta glycoside is slightly less soluble than the orthoacetate. The melting point of the pure methyl heptaacetyl-4-(*β-d*-glucosido)-*β-d*-mannopyranoside, of which about 2 g is obtained, is 178° C, and the rotation is $[\alpha]_D^{20}=-23.2°$ (chloroform, $c=3$).

A small quantity (0.5 g) of methyl heptaacetyl-4-(*β-d*-glucosido)-*α-d*-mannoside[2] is obtained from the original mother liquor after the orthoacetate and the acetylated beta glycoside have been separated. Methyl heptaacetyl-4-(*β-d*-glucosido)-*α-d*-mannopyranoside melts at 185° C and gives $[\alpha]_D^{20}=+29.3°$ (chloroform, $c=2$).

NOTES

[1] This method may be used for the preparation of both orthoacetates and *β*-methyl glycosides. Orthoacetates are produced in good yield by application of the method to halogeno-acetates which have *trans* configurations for the halogen and adjacent acetyl groups [6].

[2] The proportions of the products obtained vary with the experimental conditions. By conducting the reaction at the temperature of boiling methyl alcohol, Haworth, Hirst, Streight, Thomas, and Webb [28] found that the acetylated alpha glycoside crystallizes readily.

[3] Prepared as described on page 514.

[4] The orthoacetate derivatives are very reactive in the presence of traces of acids. Hence all solvents should be acid-free.

(k) METHODS FOR REMOVING ACETYL GROUPS

(1) Catalytic Barium Methylate Method. The catalytic barium methylate method originated by Isbell [29] is one of the most satisfactory methods for the deacetylation of the acetylated sugars and related substances. It resembles the sodium methylate method of Zemplén [30]. In both methods the alcoholate acts catalytically and merely facilitates the conversion of the acetyl groups to methyl acetate. Barium methylate is more convenient than sodium methylate because the barium may be removed readily and stock solutions may be purified before use by filtration to remove any barium hydroxide or carbonate. The reagent is prepared by adding powdered barium oxide to absolute methyl alcohol. The barium oxide reacts with the alcohol, forming barium methylate and barium hydroxide. The barium hydroxide is insoluble in the alcoholic solution and is separated by filtration. The strength of the filtered solution is ascertained by titration with 0.1 *N* aqueous sulfuric acid. The method is illustrated by the following example:

Deacetylation of methyl heptaacetyl-4-(β-d-glucosido)-β-d-mannopyranoside [26, 29].—Dry methyl heptaacetyl-4-(*β-d*-glucosido)-*β-d*-mannopyranoside (1.5 g) is dissolved in 30 ml of cold anhydrous methyl alcohol. Two milliliters of 0.4 *N* barium methylate solution in methyl alcohol is added, and the solution is allowed to stand in the refrigerator for 24 hours. After the solution has been tested for excess barium methyl-

ate,* the barium is precipitated by the addition of an equivalent quantity of sulfuric acid, or by carbonation. The precipitate is removed by filtration and the filtrate evaporated to a thick sirup which is allowed to crystallize. The crystalline mass is triturated with absolute alcohol and after separation weighs about 0.7 g. Two recrystallizations from ethyl alcohol yield pure methyl 4-(*β-d*-glucosido)-*β-d*-mannopyranoside hemihydrate, which melts at 229° C and gives $[\alpha]^{20}_{D}=-48.5°$ (water, $c=4$). Other acetylated sugar derivatives may be deacetylated in similar manner.

(2) Rapid Deacetylation with Hot Sodium Methylate.—The acetyl-glycosides, acetyl-alcohols, and other acetylated products without a free reducing group are rapidly deacetylated by a small amount (one six-hundredth of the theoretical quantity) of sodium or barium methylate at the boiling point of the methyl alcoholic solution of the substance. The amount of sodium or barium acetate formed is so small that for ordinary purposes it is not separated. The method is advantageous for acetylated substances of low solubility, but it cannot be used for substances having a free reducing group or for those sensitive to alkali. The method is illustrated by the following example:

Deacetylation of pentaacetylsalicin [31].—To 80 ml of absolute methyl alcohol, 20 g of pentaacetylsalicin and 4 ml of 0.1 *N* sodium methylate solution are added and the mixture is boiled for 5 to 10 minutes on a water bath. The cool solution, upon standing overnight, deposits about 10 g of salicin (87 percent of theory), which melts at 201° C.

(3) Deacetylation with an Excess of Alkali.—If the sugar derivative contains toluenesulfonyl or other groups which react stoichiometrically with barium or sodium methylate in methyl alcohol to form salts, an excess of alkali must be used. Barium hydroxide in aqueous solution [32], barium methylate in alcoholic solution [33], and sodium hydroxide in acetone [34] have been employed.

(I) QUANTITATIVE DETERMINATION OF ACETYL GROUPS

Since the percentages of carbon and hydrogen in the various acetyl derivatives of the carbohydrates differ only slightly, the number of acetyl groups in a carbohydrate derivative is usually determined by titration of the acetic acid formed either directly or indirectly by the hydrolysis of the acetyl groups. The determination may be conducted by several methods, which will be considered in three groups: (1) methods which depend on hydrolysis in alkaline solution, (2) methods which depend on hydrolysis in acid solution, and (3) methods which depend on the production and distillation of ethyl acetate.

The methods employing alkaline hydrolysis are applicable to the determination of acetyl groups in carbohydrate derivatives which under the conditions of the method do not give other acidic or basic decomposition products. By conducting the hydrolysis at 0° C, as described by Brauns [35], decomposition of the sugar is largely avoided and satisfactory results can be obtained with ketoses and other sugars which are relatively sensitive to alkalies. But in some cases, as for

*Since moisture or acids in the original sirup will decompose the barium methylate, it is well to test the deacetylated mixture to see if an excess of barium methylate is present. This may be done by diluting a few milliliters with water and adding several drops of phenolphthalein solution. A definite red color indicates a sufficient excess. If the test is not positive, add more barium methylate solution to the deacetylation mixture and allow 24 hours more for the deacetylation to be completed.

example with tetraacetyl-*d*-ribosido-dihydroxyacetone [36], the alkali, even at 0° C, results in the formation of acidic decomposition products; hence, the results obtained by alkaline hydrolyses are considerably greater than the theoretical values. Certain orthoester groups are relatively stable to alkaline hydrolysis but are very sensitive to acid hydrolysis. Consequently the orthoester groups can be determined by the difference in the results obtained from hydrolyses in acid and in alkaline solution. In the event that the substance contains acetyl groups attached to nitrogen, the ethyl acetate method of Perkin [37] as modified by Freudenberg and Harder [38] gives the combined *O*-acetyl and *N*-acetyl groups, while the alkaline hydrolysis at 0° C gives only the *O*-acetyl [39]. In the ethyl acetate method the acetyl derivative is heated in acid solution with ethyl alcohol, the ethyl acetate which is formed is distilled and saponified with standard alkali.

(1) Determination of Acetyl Groups by Alkaline Hydrolysis.

Method [37].—A 0.4-g sample of finely powdered tetraacetylfructose is shaken with 75 ml of 0.1 *N* sodium hydroxide at 0° C. The saponification is complete in 2 to 5 hours, when a clear solution is obtained. The excess of sodium hydroxide is titrated with 0.1 *N* sulfuric acid (phenolphthalein indicator). The difference in the amount of alkali added and the acid used in the titration gives the amount of acetic acid formed. The results usually agree with the theoretical value within 0.5 percent.

The more insoluble acetylated sugars and glycosides dissolve very slowly in aqueous sodium hydroxide and require a long time for saponification. This difficulty may be overcome by the following procedure, which uses acetone as a solvent [40]:

One-half gram of the substance is dissolved in 50 ml of acetone. The solution is cooled in an ice-and-salt mixture and 100 ml of 0.1 *N* aqueous potassium hydroxide is added dropwise. The solution is kept for 2 hours at the temperature of the ice-and-salt mixture. Then the excess alkali is titrated with 0.2 *N* hydrochloric acid. A blank control test is run and the results are corrected for its value.

(2) Determination of Acetyl Groups by Acid Hydrolysis.

Method [41].—A half-gram sample of the finely powdered substance is mixed with 100 ml of 0.25 *N* sulfuric acid and boiled for 5 hours under a reflux condenser. The solution is cooled and titrated with 0.1 *N* sodium hydroxide. The amount of acetic acid formed by the hydrolysis of the acetyl groups is equal to the difference between the amount of sulfuric acid added and the amount of alkali used.

(3) Determination of Acetyl Groups by the Ethyl Acetate Method.

Method [38].—The determination is made in the apparatus illustrated in figure 111. Flask A has a volume of 100 ml and B a volume of 150 ml. The tubes F and G must have a minimum inside diameter of 5 mm. The weighed sample (0.3 to 0.4 g), 30 ml of absolute alcohol, 5 g of *p*-toluenesulfonic acid, and a few boiling stones are introduced into flask A, and 10 ml of absolute alcohol is placed in flask B. Water is allowed to flow through the condensers C, D, and E. Flask B is cooled in an ice bath, and flask A is heated by a water bath at 100° C while its contents are allowed to reflux for 10 minutes. The bath temperature is lowered to 95° C (at which point it is kept during the subsequent operations), the reflux condenser, C, is emptied of

water, and the contents of flask A are allowed to distill for 15 minutes into flask B. Then 20 ml of absolute alcohol is introduced into flask A from the dropping funnel. The contents of flask A are refluxed for 10 minutes while water again flows through condenser C. Condenser C is then emptied and the material in flask A distilled into flask B for 10 minutes. With condenser C still empty, 20 ml of absolute alcohol is added dropwise to flask A over a period of 15 minutes while simultaneous distillation takes place. The distillation is continued

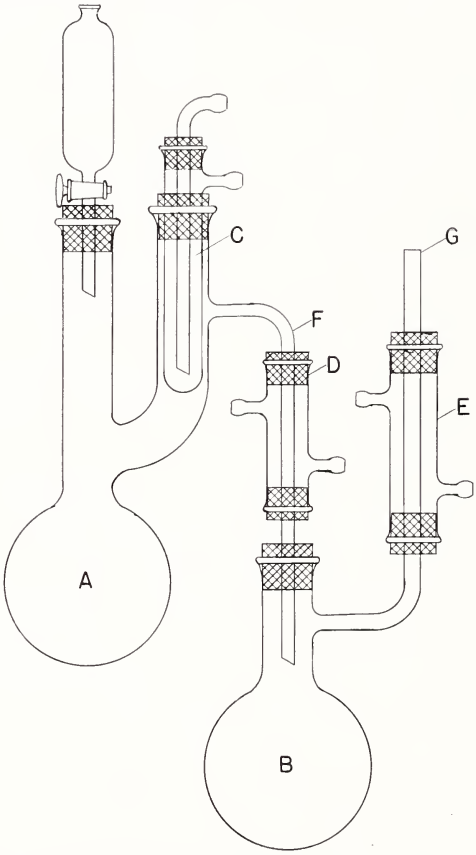


FIGURE 111.—*Apparatus for the determination of acetyl groups by the ethyl acetate method.*

for 10 minutes.[1] When the distillation is finished, 30 ml of 0.2 *N* sodium hydroxide [2] is added to flask B through the tube of condenser E. The temperature of flask A is kept at 80° C, the cold bath of flask B is replaced by a hot-water bath, and the contents of flask B are refluxed for 10 minutes. Flask B is again cooled and removed from the apparatus. After the contents have been diluted with 30 ml of water, they are titrated with 0.2 *N* sulfuric acid (phenolphthalein indicator). A blank control determination is run, and the titration is corrected for its value. Freudenberg and Harder state that the normal deviation from the theoretical value is −0.1 to +0.4 percent.

NOTES

[1] The experimental conditions as given are suitable for most sugar derivatives. In case the sample contains acetyl groups attached to nitrogen, the temperature of the bath for the flask A is kept at 100° C during the entire esterification reaction and the distillations. It is changed only during the final saponification, which is carried out as described in the *O*-acetyl directions at 80° C. The first refluxing time is lengthened from 10 minutes to 45 minutes and the second from 10 minutes to 30 minutes.

[2] The standardization of the sodium hydroxide solution is made by diluting a definite volume with an equal amount of water, adding 2 volumes of alcohol, and titrating with 0.2 *N* sulfuric acid, using phenolphthalein indicator.

(4) Determination of Acetyl Groups and Halogen in Halogeno-acetyl Derivatives.—The analytical results obtained by alkaline or acid hydrolysis of halogeno-acetyl sugars represent the total number of acid groups. However, a quantitative determination of the halogen may easily be made on the hydrolyzed solution. If alkaline saponification is employed, the excess alkali is titrated with standard nitric acid. The halogen in the solution is then determined in the conventional manner by precipitation as silver chloride, bromide, or iodide, or as calcium fluoride.

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3. HALOGENO-ACETYL DERIVATIVES

General characteristics.—Since the chloro- and bromo-acetyl derivatives may be used for the synthesis of compound sugars and for the preparation of other substances, they rank among the most important sugar derivatives. The alpha derivatives may be prepared by treating the acetyl sugars with the corresponding hydrogen halides, preferably in acetic acid solution or by treating the acetyl sugars with phosphorus pentachloride, titanium tetrachloride, or other suitable halide. Under mild conditions the glycosidic acetyl group is replaced and the alpha halogen derivative is obtained. Prolonged treatment and higher temperatures result in the formation of dihalogen substitution products and in complex reactions which give new sugars of different configuration. The beta-chloro-acetyl derivatives are prepared by treating the alpha-bromo-acetyl derivatives with silver chloride.

The fluoro- and chloro-acetyl derivatives are usually stable and may be kept for long periods, but the bromo-, and particularly the iodo-acetyl derivatives tend to decompose at room temperature. The stability of the halogeno-acetyl derivatives decreases in the order of F, Cl, Br, and I, while the reactivity increases in the same order.

Although general methods of halogenation can be applied in many cases, modifications of these general methods are often necessary in order to obtain the desired derivatives in crystalline condition. This is especially the case for the halogeno-acetyl derivatives of fructose, mannose, maltose, and melibiose. Thus Fischer and Oetker [1] were not able to prepare crystalline bromo-tetraacetylmannose, while Micheel and Micheel [2], by a slight modification of their procedure, obtained the crystalline compound. The special procedure necessary to induce bromo-heptaacetylmaltose to crystallize is given by Brauns [3].

(a) PREPARATION OF FLUORO-DERIVATIVES

(1) 1-Fluoro-2,3,4,6-tetraacetyl-*α*-*d*-glucose.

Method [4].—The preparation is best carried out in a copper apparatus consisting of a retort, water-jacketed condenser, and receiver, which are connected by ground joints. The condenser is cooled with ice water and the receiver by an ice-salt bath. About 80 g of dry potassium hydrogen fluoride [1] is placed in the retort and 10 g of pentaacetyl-*β*-*d*-glucose in the receiver. The apparatus is connected, the retort is heated to a red heat, and the hydrogen fluoride distilled into the pentaacetylglucose over a period of about 30 minutes.[2] The cold liquid in the receiver is then poured into a separatory funnel containing ice, water, and chloroform. The mixture is shaken and the chloroform separated. The aqueous layer is extracted several times with chloroform. The combined extract is washed several times with water and dried with anhydrous sodium sulfate. The chloroform solution is evaporated to a sirup which, after the addition of petroleum ether, yields crystalline 1-fluoro-2,3,4,6-tetraacetyl-*α*-*d*-glucose. The crystalline mass is dissolved in a small amount of hot ethyl alcohol and the solution is filtered and allowed to cool, whereupon crystallization

takes place. About 4 g of the crystalline substance is obtained, which may be purified by several recrystallizations from hot ethyl alcohol.

1-Fluoro-2,3,4,6-tetraacetyl-α-*d*-glucose melts at 108° C and gives $[\alpha]_D^{20} = +90.1°$ (chloroform, $c=3$).

NOTES

[1] A supply of dry potassium hydrogen fluoride is prepared by dehydrating commercial potassium hydrogen fluoride. This is advantageously performed by heating the crushed salt gradually to 140° C in a vacuum oven. The dry salt is stored in copper beakers in a vacuum desiccator. Recently anhydrous hydrofluoric acid in iron containers has been put on the market and could advantageously be used. Precautions for handling anhydrous hydrofluoric acid are given by Ruff and Plato [5]. Adequate ventilation should be provided.

[2] The amount of hydrogen fluoride produced may be determined by weighing the receiver before and after the distillation. About 20 g should be condensed in the receiver.

(b) PREPARATION OF CHLORO-DERIVATIVES

(1) 1-Chloro-2,3,4,6-tetraacetyl-α-*d*-glucose.

Method [6].—Ten grams of dry pentaacetyl-β-*d*-glucose dissolved in 70 g of purified chloroform [1] is mixed with a solution of 4.9 g of titanium tetrachloride in 25 g of purified chloroform. The yellow precipitate which forms dissolves after shaking, with the simultaneous liberation of heat. The solution is refluxed on a water bath for 3 hours, during which time care is taken to exclude moisture. The yellow solution is cooled and mixed with ice water. The colorless chloroform layer is washed several times with water, dried with calcium chloride, and evaporated under reduced pressure. The colorless sirup is dissolved in absolute ether, and the solution is saturated with petroleum ether. After the introduction of seed crystals,[2] crystallization takes place. About 7 g of crystalline material separates, and from the mother liquor another 1.5 g may be obtained. 1-Chloro-2, 3, 4, 6-tetraacetyl-α-*d*-glucose melts at 75° to 76° C and gives $[\alpha]_D^{20} = +166.1°$ (chloroform, $c=2$).

NOTES

[1] USP chloroform is washed several times with water, dried with calcium chloride, and distilled over phosphorus pentoxide.

[2] Seed crystals are obtained by stirring a little of the sirup with absolute alcohol.

(2) 1-Chloro-2,3,4,6-tetraacetyl-α-*d*-mannose.

Method [7].—Fifteen grams of crystalline pentaacetyl-β-*d*-mannose is dissolved in 30 ml of dry chloroform in a glass-stoppered Erlenmeyer flask, and 4 g of dry (sublimed) aluminum chloride and 9 g of phosphorus pentachloride are added. The mixture is slightly warmed on the steam bath in order to accelerate the reaction. In about 1 hour nearly all the aluminum chloride and phosphorus pentachloride go into solution and the mixture turns slightly green. The reaction product is then cooled, poured into ice water, and the product is extracted with chloroform. The chloroform extracts are washed several times with ice water, dried with anhydrous sodium sulfate, and evaporated in vacuo. The sirupy residue may be dried in a vacuum desiccator over paraffin wax in order to remove traces of chloroform. When the dry colorless residue is stirred with a small amount of petroleum ether, crystallization takes place. The product is recrystallized by reducing it to a powder which is extracted, first with a

100-ml portion of petroleum ether (which is kept separate as it contains most of the impurities), and then four times with 200-ml portions. By evaporating the petroleum ether in air, about 9 g of crystals is obtained. 1-Chloro-2, 3, 4, 6-tetraacetyl-α-*d*-mannose melts at 81° C and gives $[\alpha]_D^{20}=+89.9°$ (chloroform, $c=2$).

(c) PREPARATION OF BROMO-DERIVATIVES

(1) 1-Bromo-2,3,4,6-tetraacetyl-α-*d*-glucose.

Method [8, 9][1].—A mixture of 200 g of pentaacetyl-β-*d*-glucose[2] and 130 ml of a glacial acetic acid solution of hydrogen bromide (saturated at 0° C) [3] is prepared at room temperature, and the solution is allowed to stand for 2 hours. The solution is then diluted with 800 ml of chloroform, poured into 3 liters of ice and water, and stirred rapidly.[4] The chloroform layer is separated and the aqueous phase extracted once more with 200 ml of chloroform. The chloroform extracts are washed twice with ice water, dried with calcium chloride, and evaporated in vacuo [5] to a thick sirup which is taken up with 500 ml of absolute ether. Petroleum ether is added until a second liquid phase begins to appear and crystallization is allowed to take place.[6] The dried product weighs 150 to 160 g. The pure substance melts at 88° to 89° C. The material obtained at this point is sufficiently pure to be used for most purposes. However, recrystallization can be carried out by dissolving the product in the minimum amount of warm alcohol-free chloroform and then adding absolute ether. 1-Bromo-2,3,4,6-tetraacetyl-α-*d*-glucose melts at 88° to 89° C and gives $[\alpha]_D^{20}=+197.8°$ (chloroform, $c=2$).

NOTES

[1] The method as given has been worked out by B. Helferich and E. Günther, who have modified in some details the original method of E. Fischer and H. Fischer.

[2] This material may be prepared by the sodium acetate method given on page 488.

[3] A 30 to 32 percent solution of hydrogen bromide in glacial acetic acid may be obtained from chemical-supply dealers.

[4] The 1-bromo-acetyl derivatives generally decompose readily. Therefore it is necessary that the extraction be carried out rapidly and that a low temperature be maintained by adding ice. A large volume of water is desirable in order that the hydrobromic acid be as dilute as possible.

[5] The bath temperature should be kept below 45° C.

[6] The product decomposes fairly readily at room temperature. If it is to be used for further preparatory work, it should not be separated from the mother liquor until the day it is needed. Until that time the unfiltered crystals and mother liquor should be kept at 0° C. The dry crystalline substance may be kept for a considerable time at 0° C if placed over sodium hydroxide in a desiccator and spread in a thin layer.

(2) 1-Bromo-2,3,4,6-tetraacetyl-α-*d*-talose.

Method [10].—Ten grams of pentaacetyl-β-*d*-talose is dissolved in 50 ml of glacial acetic acid containing 38 percent of hydrobromic acid and 2 ml of acetic anhydride at 0°C. After the acetate has dissolved, the solution is allowed to stand for several hours at room temperature. Chloroform (60 ml.) is then added, and the solution is poured into a mixture of ice and water and extracted several times with chloroform. The extracts, washed several times with ice water and cold sodium bicarbonate solution, and dried with anhydrous sodium sulfate, are evaporated in vacuo to a thin sirup which is taken up with toluene and again evaporated to a sirup. The sirup is mixed with a small

quantity of dry ether, whereupon crystallization takes place. After several hours about 7 g of crystalline 1-bromo-2,3,4,6-tetraacetyl-α-*d*-talose separates and from the mother liquors about 0.5 g more may be obtained. The substance is recrystallized from warm dry ether. 1-Bromo-2,3,4,6-tetraacetyl-α-*d*-talose melts at 84°C and gives $[\alpha]_D^{20}=+165.6°$ (chloroform, $c=4$).

(d) PREPARATION OF IODO-DERIVATIVES

(1) 1-Iodo-heptaacetyl-4-(β-*d*-glucosido)-α-*d*-mannose.

Method [11].—Eight grams of octaacetyl-4-β-glucosido-β-*d*-mannose is dissolved in 16 ml of dichloromethane in a large Pyrex test tube and cooled in an ice-and-salt bath. A slow stream of dry hydrogen iodide is passed through the solution for one-half hour. The solution is poured into a cold crystallizing dish and evaporated under a glass jar by means of a rapid current of dry air. The sirup left after evaporation is extracted with petroleum ether by stirring and pouring off the solution. This procedure is repeated several times. Anhydrous ether is added to the residue, and by rubbing with a glass rod the sirup may be brought to crystallization. The crystals are washed with ether. They are recrystallized by dissolving in a small amount of alcohol-free ethyl acetate and adding ether and finally petroleum ether until turbidity appears. The substance crystallizes in small clusters of needles.[1] It melts with decomposition at 140°C and gives $[\alpha]_D^{20}=+111.50°$ (chloroform, $c=2$).

NOTE

[1] The iodo-acetyl sugars are not very stable, but if kept in a thin layer in a desiccator over sodium hydroxide at 0°C they may be stored for several weeks.

(e) TRANSFORMATION OF THE ACETATE OF ONE SUGAR TO THE HALOGENO-ACETATE OF ANOTHER SUGAR

(1) Conversion of Octaacetylcellobiose to Fluoro-hexaacetylglucosidomannose, (1-fluoro-hexaacetyl-4-(β-*d*-glucosido)-α-*d*-mannose).

Method [1] [11, 12].—Octaacetylcellobiose is fluorinated according to the method described for the preparation of fluoro-tetraacetylglucose. In this case, however, 200 g of the cellobiose derivative and 2 kg of potassium hydrogen fluoride are used. The distillation requires about 2 hours and about 400 g of hydrogen fluoride is obtained. The receiving vessel containing the octaacetylcellobiose and the hydrogen fluoride, after standing at room temperature for 5 hours, is cooled in an ice-and-salt bath and the contents poured into a large separatory funnel containing water, cracked ice, and chloroform. The chloroform extract is dried, concentrated in vacuo, and the chloroform-free sirup dissolved in methyl alcohol. The mixture solidifies gradually to a thick mass of white crystals which are separated after standing overnight. A second crop is obtained from the mother liquors. The total yield is more than 30 g. The recrystallization of 1-fluoro-hexaacetyl-4-(β-*d*-glucosido)-α-*d*-mannose is easily accomplished from hot methyl alcohol, from which it separates in small needles on cooling. The pure compound melts at 145°C (not sharply) and gives $[\alpha]_D^{20}=+20.8°$ (chloroform, $c=3$).

The mother liquor is evaporated in vacuo to a thick sirup from which 4-glucosidomannose is obtained by acetylating the sirup and

crystallizing octaacetyl-4-glucosidomannose from the mixture. The acetylation is conducted by the zinc chloride method given on page 489. About 35 g of pure octaacetyl-4-(β-*d*-glucosido)-α-*d*-mannose is obtained.

NOTE

[1] Occasionally an acetylated sugar may be converted to the halogeno-acetate of another sugar by treatment with a very active halogenating reagent. However, this type of reaction does not appear to be generally applicable.

(2) Conversion of Octaacetyllactose to Chloro-heptaacetylneolactose, (1-Chloro-heptaacetyl-4-(β-*d*-galactosido)-*d*-altrose).

Method [13, 14].—One hundred grams of powdered anhydrous aluminum chloride and 50 g of phosphorus pentachloride are added to 50 g of octaacetyllactose dissolved in 350 ml of alcohol-free anhydrous chloroform in a 2-liter flask. The mixture is shaken for a minute or two, the flask is connected with a reflux condenser, and the contents are heated to gentle boiling for 20 minutes. The mixture is cooled and the chloroform layer is poured into 5 liters of ice and water. The residue is also carefully decomposed with ice water and the aqueous solution is extracted with chloroform. The combined chloroform extracts are washed with ice water, dried with calcium chloride, and concentrated in vacuo to a thick sirup. This is taken up in 400 ml. of dry ether and allowed to stand for several days in the refrigerator for crystallization to take place. The crystals, which consist of 1-chloro-heptaacetyllactose and 1-chloro-heptaacetylneolactose, are collected on a filter and washed with dry ether. The crystals are then trituated with 100 ml of cold ethyl acetate. The chloro-heptaacetyllactose goes into solution and leaves a residue of crude chloro-heptaacetylneolactose. This is recrystallized by dissolving it in a small quantity of chloroform and adding several volumes of ether. The yield is about 16 to 22 g. 1-Chloro-heptaacetylneolactose melts at 182°C and gives $[\alpha]_D^{20}=+71.2°$ (chloroform, $c=1$). 1-Chloroheptaacetyllactose (melting point, 120°C) is recovered from the ethyl acetate extract.

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4. BENZOYL DERIVATIVES

General characteristics.—The benzoyl derivatives of the sugars were first prepared by application of the Schotten-Baumann reaction, using sodium hydroxide and benzoyl chloride, but it is difficult to

produce complete benzoylation by this method. By using quinoline, or better, pyridine and benzoyl chloride, complete benzoylation is obtained. By this method α-*d*-glucose gives the pentabenzoyl-α-*d*-glucose, and β-*d*-glucose gives the beta isomer. Fructose gives tetrabenzoyl furanose and pyranose derivatives as well as the open-chain pentabenzoyl-*keto*-fructose [1, 2].

(a) PREPARATION OF BENZOYL DERIVATIVES WITH BENZOYL CHLORIDE IN PYRIDINE SOLUTION

(1) PENTABENZOYL-*d*-GLUCOSE.

Method [3].—Dried anhydrous dextrose (10 g) is added to a cold solution of 35 ml of benzoyl chloride, 42 ml of dry pyridine, and 70 ml of dry chloroform.[1] The reaction is controlled by cooling the mixture in an ice-salt bath. When the sugar is all dissolved, the solution is allowed to stand for 18 hours at 0° C. A large quantity of chloroform is then added and the chloroform layer is washed successively in a separatory funnel with ice-cold dilute sulfuric acid, sodium bicarbonate, and water. It is then dried with sodium sulfate and evaporated in vacuo to a thick sirup which is reevaporated several more times with alcohol. The residue is taken up with alcohol containing 10 percent of pyridine and allowed to crystallize. Pure pentabenzoyl-α-*d*-glucose melts at 187° C[2] and gives $[\alpha]_D^{20} = +138.5°$ (chloroform).

The beta isomer is prepared in a similar way from beta glucose. In this case, however, the reaction, being less vigorous, is allowed to take place at 15° C and crystalline material settles out of the reaction mixture after several hours. From 50 g of β-*d*-glucose 120 g of the pentabenzoyl-β-*d*-glucose is obtained which, when pure, melts at 157° C[3] and gives $[\alpha]_D^{20} = +24°$ (chloroform).

NOTES

[1] The solution is prepared by cooling each reagent to −10° C, dissolving the benzoyl chloride in an equal volume of chloroform, and adding this to a solution of the pyridine in 35 ml of chloroform.

[2] Levene and Meyer recrystallized the material, first from ethyl alcohol containing 5 percent of pyridine and then from pure alcohol.

[3] A considerable number of recrystallizations from chloroform and ethyl acetate are necessary in order to obtain pure material.

(b) REFERENCES

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5. CARBONATE DERIVATIVES

General characteristics.—The sugar carbonates are well-defined and easily isolated products which are similar to the acetone sugars in many respects. The carbonate group may be removed by alkaline hydrolysis without disturbing acetone or glycosidic groups. On the other hand, the carbonyl group is more resistant to acid hydrolysis than the acetone group [1]. These properties make the carbonates useful intermediates for the production of other derivatives. The methods of preparation and properties are illustrated by the examples which follow.

(a) PREPARATION OF CARBONATES WITH CARBONYL CHLORIDE IN PYRIDINE SOLUTION

(1) 2,3-5,6-*d*-MANNOSE DICARBONATE.

Method [1].—Six grams of *d*-mannose is dissolved in 20 ml of pyridine, and the solution is vigorously stirred in an ice bath while a fairly rapid current of carbonyl chloride is passed into it. After about 45 minutes, ice water is added and the amorphous carbonate which separates is discarded. The clear solution is neutralized with an excess of barium carbonate and evaporated to a small volume under diminished pressure to remove the pyridine. The resulting solution is filtered and extracted many times with ethyl acetate. On evaporation the ethyl acetate extract gives about 0.5 g of *d*-mannose dicarbonate which is recrystallized from water. The substance melts at 122° to 123°C, and gives $[\alpha]^{21}_{578}=+26°$ (acetone, $c=1$).

(b) PREPARATION OF CARBONATES WITH CARBONYL CHLORIDE IN ACETONE SOLUTION

(1) MONOACETONE-*d*-GLUCOSE MONOCARBONATE

Method [2].—Gaseous carbonyl chloride is introduced into a suspension of glucose (8 g) in dry acetone (70 ml) under vigorous mechanical stirring until all the glucose has dissolved (3 hours). After being kept overnight, the solution is neutralized by agitation with basic lead carbonate, and filtered, and the residue washed with acetone. The combined filtrate and washings are evaporated nearly to dryness at 35°C and the resulting crystalline monoacetone-*d*-glucose monocarbonate is separated (about 3 g). The product recrystallized from ethyl alcohol sinters at 215°C and melts with decomposition and effervescence at 223° to 224° C. Monoacetone-*d*-glucose monocarbonate shows $[\alpha]^{20}_{578}=-36°$. The mother liquors yield considerable monoacetoneglucose and diacetoneglucose.

(c) REMOVAL OF THE CARBONATE GROUPS

(1) METHYL α-*d*-MANNOFURANOSIDE FROM METHYL 2,3-5,6-α-*d*-MANNOSIDE DICARBONATE.

Method [1].—The dicarbonate of methyl α-*d*-mannofuranoside dissolved in a little acetone is warmed gently with an excess of barium hydroxide solution. Barium carbonate is precipitated and after removal of the excess barium hydroxide by means of carbon dioxide treatment, and filtration, the filtrate is evaporated at 45° C; the residue is extracted with ethyl acetate or methyl alcohol. Evaporation of the extract gives crystalline methyl α-*d*-mannofuranoside in 95 percent of the theoretical yield. The product is recrystallized from methyl alcohol containing ether. Methyl α-*d*-mannofuranoside forms colorless needle-like crystals which melt at 118° to 119° C and give $[\alpha]^{20}_{D}=+113°$ (water, $c=1$).

(2) ETHYL β-*d*-GLUCOFURANOSIDE.

Method [2].—Ethyl-5, 6-β-*d*-glucofuranoside monocarbonate is dissolved in an equivalent quantity of 0.25 *N* sodium hydroxide (2 moles of alkali for each mole of the compound). After standing for several hours in the refrigerator, the solution is evaporated to dryness under diminished pressure at 35° C and the residue extracted several times with ethyl acetate. The residue obtained from evaporation of the ethyl acetate solution crystallizes when kept in a vacuum desiccator

containing phosphoric oxide. It is very hygroscopic. The recrystallization is effected by dissolving the crystals in dry ethyl acetate containing a trace of ethyl alcohol, and then adding dry ether until a slight turbidity appears. The solution is kept for several days at −10° C, and the large clusters of crystals which then accumulate (yield, 85 to 90 percent) are washed with dry ethyl acetate, drained on porous tile, and kept over phosphoric oxide in a vacuum. Ethyl-β-*d*-glucofuranoside melts at 59° to 60° C and gives $[\alpha]_D^{26} = -86°$ (water, $c=1$).

(d) REFERENCES

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6. *p*-TOLUENESULFONYL DERIVATIVES

General characteristics.—Condensation products of the sugar with *p*-toluenesulfonyl chloride are made by treating the sugar or sugar derivative with *p*-toluenesulfonyl chloride in the presence of pyridine or alkali. The *p*-toluenesulfonyl (tosyl) group so introduced is stable to weak acids and to the conditions required for acetylation, benzoylation, and methylation. Tosyl groups may be replaced, however, with hydroxyls by reduction with sodium amalgam. The tosyl group can be replaced by treatment with sodium methylate; this results in an anhydro sugar formed with Walden inversion. The anhydro derivatives are readily hydrolyzed and thus provide a means for the preparation of hitherto rare and inaccessible sugars [1]. A discussion of the Walden inversion and the steric factors which influence the formation and cleavage of the anhydro derivatives was given by Isbell [2]. A tosyl group on the terminal carbon may be replaced with iodine by treating the tosyl compound in acetone solution with sodium iodide. A nitrate group may be quantitatively substituted for the iodine atom and in turn a hydroxyl group may be substituted for the nitrate group [3]. This procedure provides a method for the identification and estimation of primary alcoholic groups and for the preparation of sugar derivatives with unsubstituted primary alcoholic groups. The pentose mercaptals react with one equivalent of *p*-toluenesulfonyl chloride to give pentose tosyl mercaptals. Since the hydroxyl on carbon 5 is blocked, these compounds readily yield furanose derivatives.

(a) PREPARATION OF TOSYL DERIVATIVES WITH *p*-TOLUENESULFONYL CHLORIDE IN PYRIDINE SOLUTION

(1) 5-Tosyl-monoacetone-β-*l*-rhamnose.

Method [4].—Monoacetone-β-*l*-rhamnose (5 g) is dissolved in 25 ml of dry pyridine, and 4.81 g (1.1 moles) of *p*-toluenesulfonyl chloride is dissolved in 10 ml of dry alcohol-free chloroform, and the two solutions are mixed at 0° C. The solution is kept in an ice bath for about 1 hour and then at room temperature for 12 hours more. Water (1 ml) is then added and the mixture is thoroughly shaken and allowed to stand for 30 minutes. More chloroform is added and the chloroform layer is washed at 0° C twice each with water, 10-percent sulfuric acid, saturated sodium bicarbonate, and finally again with water. The extract, after drying with calcium chloride, is evaporated under reduced pressure to a thick sirup which is re-

evaporated with toluene. The residue is dissolved in toluene and petroleum ether is added to saturation. Crystallization takes place readily and about 3.5 g of material is obtained. The pure 5-tosyl-monoacetone-β-*l*-rhamnose melts at 92° to 93° C and gives $[\alpha]_D^{24} = +29.1°$ (chloroform).

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7. METHYL ETHERS

General methods.—The stability of methyl ethers of the sugars in the presence of acid or alkali has made them very useful in structural studies. Purdie and Irvine [1] first employed silver oxide and methyl iodide as methylating agents for sugars. Aldehyde and ketone groups are oxidized by silver oxide, and hence it is necessary to convert reducing sugars into glycosides before methylating with these reagents. Three or four treatments with the reagents are frequently necessary for complete methylation.

Haworth [2] in 1915 used dimethyl sulfate and 30-percent aqueous sodium hydroxide. These reagents are less expensive than those used previously and are better adapted to the first stages of the methylation because of the solubility of the sugars and glycosides in aqueous solution.

Sodium and potassium salts have been used as intermediates in the preparation of methyl derivatives of carbohydrates. Freudenburg and Hixon [3] prepared 3-methyl-diacetone-*d*-fructose in 85- to 90-percent yield by first making the sodium salt of diacetonefructose in benzene solution and treating this salt with methyl iodide.

Fear and Menzies [4] prepared the trithallium salt of methyl α-*d*-glucoside by means of thallous hydroxide. This salt when refluxed with methyl iodide gave methyl trimethyl-α-*d*-glucoside [5]. In the presence of excess thallous hydroxide the methyl tetramethyl α-*d*-glucoside was formed.

Muskat [6] described a method for methylating sugars in which he prepared their potassium, sodium, or lithium salts in liquid ammonia (−33.4° C) and allowed this salt to react with methyl iodide. By this method the complete methylation or partial methylation is obtained in one step, depending upon the number of metallic atoms introduced. A special apparatus is required, since it is necessary to maintain anhydrous conditions at low temperatures.

(a) METHYLATION WITH METHYL IODIDE AND SILVER OXIDE

(1) METHYL 2,3,4,6-TETRAMETHYL-α-*d*-GALACTOSIDE.

Method [7].—Nineteen grams (0.1 mole) of methyl α-*d*-galactoside and 142 g (1 mole) of methyl iodide are placed in a three-necked flask equipped with a mercury-sealed mechanical stirrer and a condenser through which ice water is circulated, and sufficient hot methyl alcohol is added to dissolve the galactoside. The flask is heated in a water bath at 45° C so as to keep the methyl iodide gently refluxing, and in 10 equal portions at ½-hour intervals there is added 116 g

(0.5 mole) of silver oxide.[1] The heating is continued for 1 hour after the final addition of silver oxide. The reaction mixture is extracted with boiling absolute methyl alcohol and the solvent removed by means of vacuum distillation, the temperature finally being raised to 100° C in order to remove all traces of water.

The sirup thus obtained is dissolved in an equal weight of absolute methyl alcohol and the methylation repeated. The reaction product is extracted with ether and the solvent removed by means of vacuum distillation as before.

A third methylation is carried out, and since the partially methylated galactoside is soluble in methyl iodide, the methyl alcohol is omitted, but the same amounts of methyl iodide and silver oxide are used. The reaction mixture is extracted with ether and the final product distilled. The distillate, which boils at 136° to 137° C at 11 mm, is collected in one fraction. A higher boiling fraction upon remethylation also gives the methyl tetramethylgalactoside. The total yield is about 60 percent of the theoretical. Methyl 2,3,4,6-tetramethyl-α-*d*-galactoside gives $[\alpha]_D^{20}=+143.4°$ (water, $c=10$) and has a specific gravity of 1.107.

NOTE

[1] The silver oxide should be freshly prepared and finely divided. C. B. Young in a monograph, A General Review of Purdie's Reaction, gives the following procedure for its preparation [8]. A hot filtered barium hydroxide solution (100 g of $Ba(OH)_2.8H_2O$ in 1 liter of water) is added to a hot solution of silver nitrate (100 g of silver nitrate in 500 ml of water), and the precipitated silver oxide washed with boiling water until all excess barium hydroxide has been removed. The filtered product is dried, first on a porous plate and afterwards in an open steam oven. The oxide is powdered to facilitate drying and is kept in a desiccator until required for use.

(b) METHYLATION WITH DIMETHYL SULFATE AND SODIUM HYDROXIDE

(1) Heptamethylsucrose.

Method [2].—Sucrose (20 g) is dissolved in 10 ml of water contained in a 1-liter three-necked flask fitted with two dropping funnels, a water condenser, and a mechanical stirrer. The flask is placed in a water bath maintained at 70° C. During 1 hour 120 ml of dimethyl sulfate and 320 ml of 30-percent sodium hydroxide are added in such a way that the solution is always alkaline. The bath temperature is raised to 100° C and the reaction mixture heated for 1 hour in order to decompose the unreacted dimethyl sulfate. The solution is then cooled and extracted with chloroform. The chloroform is evaporated and the heptamethyl sucrose distilled under reduced pressure. About 15 g of heptamethyl sucrose is obtained as a colorless viscous sirup which gives a boiling point of 191° to 195° C at 0.18 mm pressure, and $[\alpha]_D^{20}=+68.5°$ (methyl alcohol, $c=6$).

(c) PREPARATION OF METHYL ETHERS FROM THE ACETATES

Dimethyl sulfate and aqueous sodium hydroxide in acetone solution may be used to prepare methyl derivatives from sugar acetates. The acetyl groups are completely replaced by methyl groups during one treatment with the methylating reagents. Compounds of high molecular weight that are difficult to methylate directly because of their insolubility are conveniently methylated by this method.

(1) Trimethylinulin.

Method [9].—Twelve grams of inulin acetate and 250 ml of acetone are placed in a 2-liter flask equipped with a mechanical stirrer. The temperature is kept at 55° C and 120 ml of dimethyl sulfate and 320 ml of 30-percent aqueous sodium hydroxide are added in portions of 12 ml and 32 ml, respectively, at 10-minute intervals. Acetone is added from time to time in such amount that the volume of the reaction mixture is 300 ml or more. An emulsion forms after the second or third addition of reagents. Immediately following the addition of the final portion of dimethyl sulfate and sodium hydroxide, 100 ml of water is added and the temperature raised to 75° C for a period of 15 minutes in order to remove the bulk of the acetone. Trimethylinulin separates as pellets or as a fine porous solid, its nature depending upon the rate of stirring. The mixture is poured into a large volume of water with rapid stirring, and the methylated inulin is collected on a filter and washed with hot water. The air-dried product is dissolved in boiling alcohol; on cooling, trimethylinulin separates as a white amorphous solid. The crude substance is purified by dissolving it in a mixture of equal volumes of chloroform and acetone and precipitating the product by the addition of petroleum ether. The yield is 95 percent of the theoretical. Trimethylinulin melts at 140° C and gives $[\alpha]_D^{20}=-55°$ (chloroform, $c=1$).

(d) METHYLATION WITH METHYL IODIDE AND A SODIUM SALT IN BENZENE OR ETHER SOLUTION

(1) 3-Methyl-diacetone-*d*-fructose.

Method [3].—Ten grams of 1, 2-4, 5-diacetonefructose and 50 ml of benzene are placed in a 100-ml pressure flask, and under anhydrous conditions an excess of sodium is added in small portions. After 3 to 4 hours, when the evolution of hydrogen is complete, the excess sodium is removed with a glass rod. The solution is reduced to a sirupy consistency by evaporation under diminished pressure, after which 11 g (2 moles) of methyl iodide is added and the mixture is allowed to stand for 24 to 28 hours at 30° to 40° C. The material is then diluted with ether, and the sodium iodide which precipitates is separated by filtration and washed with ether. 3-Methyl-diacetone-*d*-fructose crystallizes from the ether solution. The crystals are collected on a filter and washed with a little water to remove the unmethylated diacetone-fructose. The crude material is recrystallized from petroleum ether. A yield of 85 to 90 percent of the pure product melting at 115° C is thus obtained.

In the preparation of the corresponding methyl derivatives of glucose, galactose, and mannose by this procedure, 30 ml of dry ether is used as solvent in place of the 50 ml of benzene.

(e) METHYLATION WITH THALLOUS HYDROXIDE AND METHYL IODIDE

(1) Methylation of Methyl α-*d*-glucopyranoside.

Method [5].—Twelve hundred ml of 1.33 *N* thallous hydroxide is evaporated to a volume of 400 ml and while hot is poured into a solution of 38 g of methyl α-*d*-glucoside dissolved in 18 ml of water. The precipitate is filtered and dried over phosphorus pentoxide in a vacuum desiccator protected from light. Seven days are required for the drying. The dry powder (about 240 g) is heated 6 hours under a reflux condenser with 115 ml of methyl iodide. The excess methyl

iodide is evaporated and the residue is extracted with chloroform. The chloroform solution is concentrated to a sirup and fractionally distilled under reduced pressure. Barker, Hirst, and Jones [5] report three fractions: (1) Methyl tetramethyl-α-*d*-glucoside (6.2 g), boiling point 125°C at 0.01-mm pressure, $n_D^{17°}=1.4450$. On hydrolysis with 8-percent hydrochloric acid at 95°C this gave nearly quantitatively tetramethyl glucopyranose, melting point 87°C. (2) A mixture of methyl tetramethyl-α-*d*-glucoside and methyl trimethyl-α-*d*-glucoside (4.7 g), boiling point 135°C at 0.01-mm pressure, $n_D^{12.5°}=1.4522$. (3) Methyl trimethyl-α-*d*-glucoside (17.5 g), boiling point 140° to 143°C at 0.01-mm pressure $n_D^{18.5°}=1.4572$.

(f) QUANTITATIVE DETERMINATION OF METHOXYL GROUPS

The Zeisel method [10] for the determination of alkoxyl groups consists in treating an ether with boiling hydrogen iodide, whereby the following reaction takes place:
$R'OR+HI \rightarrow R'OH+RI$. The volatile iodide is collected in an alcoholic silver nitrate solution as $AgI.2AgNO_3$. When treated with

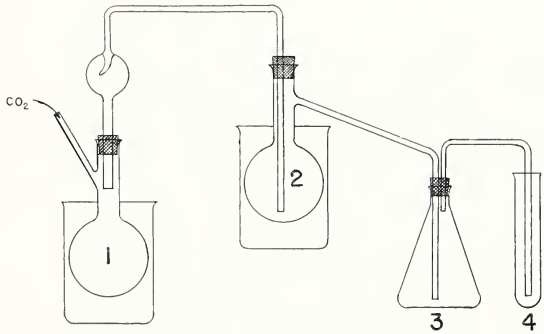

FIGURE 112.—*Apparatus for the gravimetric determination of methoxyl groups.*

water this double salt decomposes, yielding silver iodide, which is determined gravimetrically.

When sulfur is present, it is necessary to substitute pyridine for the alcoholic silver nitrate and to evaporate the pyridine solution to dryness before precipitating the iodide as the silver salt. If the compound contains an alkyl group attached to nitrogen, the *N*-alkyl group may be partially converted to the alkyl iodide. Also, in the presence of hydrogen iodide an alkyl group may be transferred from an oxygen to a nitrogen atom.

(1) GRAVIMETRIC METHOD [10].

Reagents.—Hydrogen iodide: Density, 1.7; boiling point, 125° to 127°C; 57-percent solution. *Silver nitrate solution:* About 4 g of silver nitrate is dissolved in 10 ml of water and mixed with 90 ml of absolute alcohol. The solution is kept in the dark; and before use, it is filtered through a dry filter paper and acidified with nitric acid. *Red phosphorus:* The reagent grade of red phosphorus is digested one-half hour with dilute ammonia, washed with hot water, and stored under water.

323414°—42——34

Procedure.—About 15 ml of hydrogen iodide, a boiling stone, and a trace of red phosphorus are placed in the 50-ml round-bottom flask (1) of figure 112. The flask is equipped with an inlet tube for admitting carbon dioxide, and with either an air-cooled or a water-jacketed reflux condenser held at 40° to 60°C and connected with a scrubber (2) containing a little warm water and 0.5 g of red phosphorus. This scrubber, or flask, is connected with absorption bottles (3) and (4), which contain, respectively, 20 ml and 10 ml of alcoholic silver nitrate. Before the analysis is started, a blank test is run by refluxing the hydrogen iodide while a stream of carbon dioxide is passed through the apparatus. There should be no turbidity in the silver nitrate solution during an interval of 10 minutes. After the blank test has been made, flask (1) is cooled and a 0.3 to 0.4-g sample of the material to be analyzed is introduced. The hydrogen iodide is warmed slightly and refluxed in the presence of a stream of carbon dioxide. In about 10 minutes a white precipitate of $AgI.2AgNO_3$ begins to form in the first silver nitrate container. Upon completion of the reaction, which usually requires about 40 minutes, the silver nitrate solutions are combined, diluted with several volumes of water, acidified with nitric acid, and boiled gently for several minutes. The silver iodide is then determined gravimetrically. $AgI \times 0.1322 = OCH_3$.

(2) Volumetric Method [11, 12, 13].—The alkyl halide is collected in an acetic acid solution of potassium acetate and bromine. This method, which can be used for substances containing sulfur, requires less time and a smaller sample than the gravimetric method. The following reactions take place in the bromine solution:

$$CH_3I + Br_2 \rightarrow CH_3Br + IBr.$$
$$IBr + 2Br_2 + 3H_2O \rightarrow HIO_3 + 5HBr.$$

The solution is washed into a flask containing aqueous sodium acetate, the excess bromine is removed with formic acid, potassium iodide is added, the solution acidified with sulfuric acid, and the liberated iodine titrated with 0.1 *N* thiosulfate. Each methoxyl group liberates six atoms of iodine; hence 1 ml of 0.1 *N* thiosulfate represents 0.5172 mg of methoxyl. Thus for a 10-ml titration 10 to 40 mg of a methyl sugar is sufficient.

Reagents.—Hydrogen iodide: Hydrogen iodide free from iodine may be obtained by treating constant-boiling hydrogen iodide at approximately 100°C with slightly more than the necessary quantity of 50-percent hypophosphorous acid. When the hydrogen iodide is thus treated, no free iodine is evolved and hence no red phosphorus is necessary in the scrubber, *B*. (fig. 113). *Potassium acetate:* 10-percent solution of potassium acetate in acetic acid. *Sodium acetate:* 25-percent solution. *Sodium thiosulfate:* 0.1 *N* solution.

Procedure.—A 10- to 40-mg sample of the material to be analyzed is introduced into the reaction flask, *A*, in which 5 ml of hydrogen iodide and 2.5 ml of melted analytical phenol have been placed. If a solid, the sample may be weighed on a piece of cigarette paper; if a liquid, it may be weighed and added in a small glass container. The flask is connected to the rest of the apparatus, which consists of a scrubber, *B*, containing a little water, and two receiving flasks, *C* and *D*. The receiving flasks contain 10 ml of a 10-percent solution of potassium acetate in acetic acid to which 6 drops of bromine have been added, about 6 ml in the first and 4 ml in the second flask. A

slow uniform stream of carbon dioxide is passed through the apparatus and the reaction flask is gently heated until the liquid refluxes halfway up the condenser. Ordinarily 30 to 45 minutes are required to complete the reaction and sweep out the apparatus. After the reaction is complete, the contents of the 2 receivers are washed into a 250-ml Erlenmeyer flask containing 5 ml of a 25-percent aqueous sodium acetate solution. The volume of the solution is adjusted to about 125 ml and 6 drops of 90-percent formic acid is added. Then the flask is rotated until the color due to bromine disappears, whereupon 12 more drops of formic acid is added. The mixture is allowed to stand 2 minutes, 1 g of potassium iodide and a few milliliters of 10-percent sulfuric acid are added, and after 3 minutes the liberated iodine is titrated with 0.1 N sodium thiosulfate.

A blank should be run on the reagents, as all phenol appears to contain some substance which gives a small blank. This value is to be subtracted only from the first determination made with a given charge, as the material responsible for the blank is destroyed with the first determination. If the carbon dioxide is introduced above the surface of the hydrogen iodide-phenol charge, bumping may be prevented by introducing a capillary boiling tube. Each methoxyl group liberates six atoms of iodine, and hence requires 6 moles of thiosulfate.

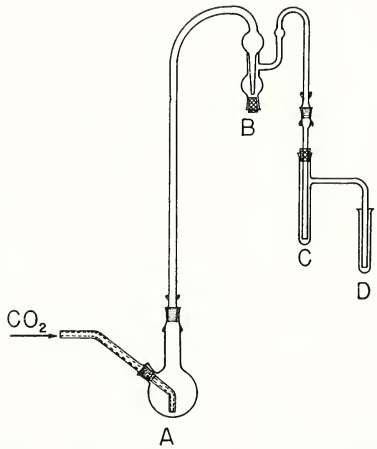

FIGURE 113—*Apparatus for the volumetric determination of methoxyl groups.*

$$\frac{\text{ml } 0.1\ N \text{ thiosulfate} \times 0.5172 \times 100}{\text{mg sample}} = \text{percentage of } OCH_3$$

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8. TRIPHENYLMETHYL ETHERS

General characteristics.—Triphenylmethyl chloride reacts with sugars and glycosides in the presence of pyridine to give triphenylmethyl ethers, which are called "trityl" derivatives. It has been

shown that triphenylmethyl chloride condenses, preferably with the primary alcohol group. However, under more severe conditions secondary alcoholic groups will react [1]. Since the trityl derivatives are stable under the conditions required for acetylation and benzoylation, and since the trityl group may be removed easily by mild acid treatment, these compounds have proved useful for the production of sugar derivatives containing free primary hydroxyl groups [2]. The trityl group may also be replaced directly by bromine or iodine atoms [3].

(a) PREPARATION OF TRITYL DERIVATIVES

(1) METHYL 6-TRITYL-α-*d*-GLYCOPYRANOSIDE.

Method [4].—One part of dry methyl α-*d*-glucoside and 1.4 parts of triphenylchloromethane (equivalent proportions) are dissolved in 8 parts of pure dry pyridine.[1] The solution is heated on a boiling-water bath for 1 hour[2] and then is allowed to cool. Water is added dropwise until the point of turbidity is reached, and the solution is allowed to stand for an hour. The solution is then poured into ice water. The sirupy layer is separated and rubbed up repeatedly with fresh portions of water. Crystallization takes place slowly. About 1.5 parts of the trityl derivative are obtained. The crude product is recrystallized from 5 parts of alcohol. When air-dried the compound contains 1.5 moles of alcohol of crystallization and melts at 80° C if heated rapidly. Methyl 6-trityl-α-*d*-glucopyranoside, when alcohol-free, melts at 151° to 152° C and gives $[\alpha]^{16}_{D}=+86.3°$ (pyridine).

NOTES

[1] Traces of water will inhibit this reaction markedly.

[2] Or allowed to stand 24 hours at room temperature. For those glycosides without a primary alcohol group a considerably longer time is required (14 days at room temperature).

(b) REMOVAL OF TRITYL GROUPS

(1) CONVERSION OF METHYL 2,3,4-TRIBENZOYL-6-TRITYL-α-*d*-GLUCOSIDE TO METHYL 2,3,4-TRIBENZOYL-α-*d*-GLUCOSIDE.

Method [4].—Two parts of methyl 2,3,4-tribenzoyl-6-trityl-α-*d*-glucoside are dissolved in 2.5 parts (by volume) of chloroform. The solution is cooled in an ice bath and is rapidly saturated with dry hydrogen chloride. After 30 minutes an excess of a saturated aqueous solution of potassium bicarbonate is mixed with the ice-cold solution. The chloroform layer is washed with water, dried with calcium chloride and evaporated in vacuo to a sirup which is taken up with a small amount of methyl alcohol. Upon standing at 0° C the solution deposits crystals of triphenylcarbinol and triphenylmethyl methyl ether. The crystals are separated and the mother liquor is evaporated again in vacuo to a thick sirup, which is dissolved in 1.5 parts (by volume) of hot absolute alcohol. Methyl tribenzoyl-α-*d*-glucoside crystallizes from the alcoholic solution in a yield of about 65 per cent and gives $[\alpha]^{19}_{D}=+131.7°$ (pyridine).

(c) QUANTITATIVE DETERMINATION OF TRITYL GROUPS

The trityl groups in a compound can be determined by their conversion to triphenylcarbinol. A weighed sample which will yield

approximately 100 mg of triphenylcarbinol is dissolved with careful trituration in 2 ml of sulfuric acid (sp gr 1.84). This solution is poured quickly into 50 ml of distilled water and allowed to stand for 30 minutes. The triphenylcarbinol is collected on a weighed Gooch crucible, washed with distilled water, and dried at 110° C to constant weight. The results can be expressed as triphenylcarbinol, or as percentage of triphenylmethyl groups according to the formula:

$$\frac{\text{Wt of triphenylcarbinol} \times 0.9347 \times 100}{\text{Wt of sample}} = \text{percentage of } C(C_6H_5)_3$$

(d) REFERENCES

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9. GLYCOSIDIC DERIVATIVES

(a) PREPARATION OF GLYCOSIDES BY FISCHER METHOD [1]

General characteristics of the method.—By treating dry methyl alcoholic solutions of the sugars with hydrogen chloride, the hydroxyl of the reducing carbon is replaced by a methoxyl group and an equilibrium is established between the alpha and beta methyl pyranosides and furanosides [2]. When other alcohols—such as ethyl, propyl, amyl, isopropyl, allyl, and benzyl—are used as solvents, the corresponding glycosides are formed. The pyranose modifications usually predominate in the equilibrium mixture; the furanose modifications are at their maximum during the early stages of the reaction. In the preparation of furanose and pyranose glycosides advantage is taken of these properties [3]. The furanosides are prepared by allowing the reaction to proceed, usually at room temperature, until the furanoside content reaches a maximum; the pyranosides are prepared by heating the alcoholic solution until equilibrium is reached. The time required for reaching the desired state varies for the different sugars.

Since the equilibrium mixture contains the alpha and beta pyranose and furanose modifications, it is often difficult to obtain crystalline products. The following methods are useful for the purification of glycosides:

(a) Acetylation of the crude glycoside mixture gives products which frequently can be separated in the crystalline state.

(b) Calcium chloride and other molecular compounds are occasionally useful for separating the isomeric glycosides [4, 5, 6, 7].

(c) Mixtures of the acetylated alpha and beta glycosides in chloroform solution are converted by titanium tetrachloride to mixtures in which the alpha isomer predominates [8].

(d) For some glycosides the selective action of enzymes may be used to remove one of the isomers from the crude mixture. By using the proper enzyme [9] (α-glucosidase or β-glucosidase, or the corresponding enzymes for other sugars) the alpha or beta methyl glycoside may be removed from a mixture of the two. This method has been successfully employed for the separation of the methyl fructosides [10].

(e) Since the methyl furanosides and their acetates can be distilled at a low pressure, distillation may be used to separate them from the less volatile pyranosides [2].

The Fischer method using methyl alcoholic hydrogen chloride is particularly suitable for preparing the methyl pyranosides. It is usually not applicable to disaccharides as hydrolysis occurs simultaneously with glycoside formation. When the sugar is insoluble in the alcohol, the method may be applied to an alcoholic solution of the halogeno-acetyl or the acetyl sugar. In this case, deacetylation and glycoside formation proceed simultaneously.

(1) METHYL *l*-ARABINOPYRANOSIDES.

Method.—[11].—One hundred grams of *l*-arabinose is refluxed for 3 hours with 1 liter of anhydrous methyl alcohol containing 1.5 percent of hydrogen chloride. The acid is neutralized with silver carbonate[1] and the solution is filtered, treated with activated charcoal, and refiltered. The filtrate is evaporated in vacuo to a thin sirup, which is allowed to crystallize. About 30 g of crude methyl β-*l*-arabinoside is obtained which is purified by an extraction with hot ethyl acetate. The residue is recrystallized from absolute ethyl alcohol. A second extraction and recrystallization give pure methyl β-*l*-arabinopyranoside, which melts at 169° C and gives $[\alpha]_D^{20}=+245.5°$ (water, $c=7$).

The mother liquor from the beta arabinoside preparation is evaporated under reduced pressure to a thin sirup which, after standing in a vacum desiccator, crystallizes slowly. The crystalline material, which is a mixture of the alpha and beta isomers, is separated and fractionally recrystallized from hot ethyl acetate.[2] The less soluble beta isomer crystallizes first and the alpha isomer accumulates in the mother liquors. Pure methyl α-*l*-arabinopyranoside melts at 131° C and gives $[\alpha]_D^{20}=+17.3°$ (water, $c=3$).

NOTES

[1] Silver carbonate is prepared by mixing a 10-percent aqueous solution of silver nitrate with a molecularly equivalent solution of sodium bicarbonate. The resulting precipitate is collected on a filter and washed with water until free from sodium salts, and then with methyl alcohol. The product is air-dried and protected from light.

[2] For other methods useful for separating glycoside mixtures, see page 513.

(2) METHYL α-*d*-ARABINOFURANOSIDE.

Method [12].—One hundred grams of powdered and sieved *d*-arabinose is shaken at 20° C with 4 liters of anhydrous methyl alcohol containing 29.2 g of hydrogen chloride (0.7 percent). Complete solution occurs after about 30 minutes, and the solution is then allowed to stand for 17 hours.[1] The acid is removed by treating the mixture with silver oxide,[2] and the excess silver is precipitated with hydrogen sulfide. The filtered solution is concentrated in vacuo to a thick sirup,[3] which is dried overnight in a vacuum desiccator. The sirup is then extracted six times with 400-ml portions of anhydrous ether.[4] The ether extract is evaporated in vacuo to a sirup which weighs about 23 g.[5] The sirup is taken up with ethyl acetate and allowed several days to crystallize.[6] The crystalline material, methyl α-*d*-arabinofuranoside, when separated and dried, weighs about 11.5 g. It is recrystallized by slowly cooling a warm ethyl acetate solution of the material to 5° C. The crystals melt at 65° to 67° C and give $[\alpha]_D^{20}=+123°$ (water, $c=1$).

NOTES

[1] Montgomery and Hudson [12] report that the solution, upon standing at 20° C, becomes nonreducing after 4.5 hours and has a specific rotation of $[\alpha]_D^{20}=+24°$. On further standing the rotation increases to a maximum value of $[\alpha]_D^{20}=+45°$ in 17 hours and thereafter decreases to $[\alpha]_D^{20}=-17°$ in 42 hours.

[2] The acid must be completely removed, since the furanosides are very unstable in the presence of acids and water.

[3] Unless a flask is used which is separable from the distilling head, it is well to transfer the solution while is it still dilute to another container in which the extraction may be readily carried out after the sirupy stage has been reached.

[4] Each extraction may be readily carried out by shaking the ether and sirup in a shaking machine for 45 minutes.

[5] This furanoside is very hygroscopic and should be kept out of contact with moist air during this and succeeding operations. Montgomery and Hudson used a cabinet (55 by 39 by 43 cm) constructed of copper and with a glass top and removable end with strip-felt closure. The other end was provided with 2 openings 13 cm in diameter into which long rubber gloves were fitted with adhesive tape.

[6] The first crystals were obtained by allowing the solution to stand at 5° C for several months.

(b) USE OF CALCIUM CHLORIDE COMPOUNDS TO SEPARATE GLYCOSIDES

(1) METHYL *d*-GULOPYRANOSIDES.

Method[1] [4].—Forty grams of α-*d*-gulose $CaCl_2.H_2O$[2] is refluxed for 6 hours with 300 ml of absolute methyl alcohol containing 4.5 g of anhydrous hydrogen chloride. The warm solution is slowly neutralized with a slight excess of finely powdered calcium carbonate. After the addition of about 1 g of decolorizing carbon, the solution is filtered. The filtrate is concentrated in vacuo to a thick sirup, which is diluted with 50 ml of absolute ethyl alcohol. In the course of several hours, a crystalline product separates. The crystals are collected on a filter and washed with a mixture of equal parts of absolute ethyl alcohol and ethyl acetate. The mother liquor is evaporated in vacuo to a sirup which is saturated with ethyl acetate, and additional crystals are obtained.[3]

The dextrorotatory crystals are combined and recrystallized from ethyl alcohol to give methyl α-*d*-guloside.$CaCl_2.2H_2O$ and $[\alpha]_D^{20}=+66.8°$ (water, $c=7$). The levorotatory crystals are combined and recrystallized to give pure methyl β-*d*-guloside.$CaCl_2.2H_2O$[4] and $[\alpha]_D^{20}=-45.7°$ (water, $c=2$).

The free glycosides are obtained by shaking the calcium chloride compound in water solution with silver oxalate, silver sulfate, or silver carbonate. The resulting insoluble calcium and silver salts are separated by filtration and the free glycoside is crystallized from the aqueous solution. Methyl α-*d*-gulopyranoside crystallizes as a monohydrate which melts at 77° C and gives $[\alpha]_D^{20}=+109.4°$ (water, $c=2$). Methyl β-*d*-gulopyranoside melts at 176° C and gives $[\alpha]_D^{20}=-83.3°$ (water, $c=3$).

NOTES

[1] Calcium chloride compounds have also proved useful for the preparation of methyl α-*d*-α-glucoheptopyranoside [5], of methyl β-*d*-mannofuranoside [6], and for the separation of the methyl 2,3,6-trimethylglucofuranosides [7]. If calcium chloride is not present in the original sugar it must be added in the appropriate quantity.

[2] The preparation of α-*d*-gulose.$CaCl_2.H_2O$ is described on page 465.

[3] In a typical experiment the first crop of crystals weighed 15 g and gave $[\alpha]_D^{20}=+60.8°$; the second crop, 3.72 g, $[\alpha]_D^{20}=+37.5°$; the third crop, 6.0 g, $[\alpha]_D^{20}=+17.3°$; the fourth crop, 3.5 g, $[\alpha]_D^{20}=-36.0°$.

[4] These compounds crystallize from solutions containing 1 mole or more of calcium chloride; compounds containing less calcium chloride are obtained under different conditions.

(c) PREPARATION OF GLYCOSIDES FROM HALOGENO-ACETYL DERIVATIVES

The Koenigs-Knorr reaction [13].—By treating certain halogeno-acetyl sugars in methyl alcoholic solution with silver carbonate, the halogen is replaced by a methoxyl to give the acetylated glycosides, of the same ring structure as that of the halogeno-acetyl sugar used. The replacement of the halogen is usually accompanied by Walden inversion, and as pointed out by Isbell [14] normal glycosides are formed in good yield from halogeno-acetyl sugars having the halogen and acetyl groups on the same side of the sugar ring, whereas ortho-acetic esters are formed from halogeno-acetyl sugars having the halogen and acetyl groups on opposite sides of the sugar ring.

Glycosides having complex aglucone groups may be prepared from the halogeno-acetates by use of various alcohols and phenols. If a solid alcohol or phenol is to be used, the substance in solution in an inert solvent such as benzene, or quinoline, is condensed, usually in the presence of silver carbonate or silver oxide, with the halogeno-acetyl sugar dissolved in a similar solvent [15,]. The addition of a dehydrating agent, such as calcium chloride or Drierite [16], frequently improves the yields of the desired product. This method has also been applied to the preparation of furanoside derivatives [17].

Pyridine, quinoline, and sodium hydroxide have been used in place of silver carbonate. By treating the halogeno-acetyl derivatives in alcoholic solution with mercury salts instead of silver salts, Zemplén and Gerecs have worked out optimum conditions for the selective preparation of either the alpha or beta ethyl cellobiosides [18]. In general, by this method the formation of alpha isomers seems to be favored by approximately equivalent concentrations of halogeno-acetate, alcohol, and mercury salt [18, 19]. Another method consists in condensing alcoholic solutions of the fully acetylated sugars in the presence of sublimed ferric chloride [20]. By the use of 1 mole of ferric chloride for each mole of the acetate, 20-percent yields of ethyl heptaacetyl-α-cellobioside are obtained.

(1) METHYL TETRAACETYL-β-*d*-GLUCOPYRANOSIDE.

Method [13].—Ten grams of bromo-tetraacetylglucose is dissolved in 150 ml of absolute methyl alcohol at room temperature and shaken with 10 g of dry powdered silver carbonate. The mixture is shaken until a halogen test of the solution is negative (about 6 hours). The mixture is filtered and the silver salts are washed with ether. The filtrate is treated with water and a little barium carbonate, and after a second filtration it is concentrated in vacuo to a heavy sirup which is extracted with ether. The combined ether extract is washed with sodium carbonate solution, then with water, and finally dried with sodium sulfate.

Methyl tetraacetyl-β-*d*-glucopyranoside crystallizes upon concentration of the solution. It is recrystallized from methyl alcohol or ligroin. The crystals melt at 105° C and give $[\alpha]_D^{20}=-18.2°$ (chloroform, $c=4$).

(d) PREPARATION OF PHENOLIC GLYCOSIDES FROM ACETYL DERIVATIVES

A very good method for preparing glycosides of phenols is that of Helferich and Smitz-Hillebrecht [21]. The phenol is melted with the

acetyl sugar in the presence of zinc chloride or *p*-toluene sulfonic a The zinc chloride customarily yields alpha glycosides, and the *p*-- cid enesulfonic acid, beta glycosides. Glycosides of polyhydric alcohols and phenols have been prepared with several sugar residues in the molecule. The method is carried out by condensing the polyhydric phenol with the acetylated sugar and then reacting the product with a bromo-acetyl sugar in an aqueous acetone solution of sodium hydroxide.

(1) Phenyl Tetraacetyl-α-*d*-glucopyranoside.

Method [21].—A mixture of 50 g of β-pentaacetylglucose, 46 g of phenol, and 12.5 g of anhydrous zinc chloride is heated in a bath at 125° to 130° C. for 45 minutes while mechanically stirred. The dark solution is allowed to cool and is then dissolved in 300 ml of benzene and several hundred milliliters of water. The benzene solution is washed with water, then several times with 2 *N* sodium hydroxide solution, and finally several times with water. The solution is dried with calcium chloride and evaporated to a thick sirup, which is dissolved in hot alcohol and allowed to crystallize. After several recrystallizations from absolute alcohol, about 13 g of pure phenyl tetraacetyl-α-*d*-glucopyranoside is obtained. The compound melts at 114° to 115° C and gives $[\alpha]_D^{20} = +168°$ (chloroform).

The phenyl α-*d*-glucopyranoside is readily prepared from this material by deacetylation, using the method of Zemplén (see p. 494).

(2) Phenyl Tetraacetyl-β-*d*-glucopyranoside.

Method [21].—A mixture of 292 g of phenol, 3.9 g of *p*-toluenesulfonic acid, and 300 g of β-pentaacetylglucose is heated for 90 minutes, while mechanically stirred, in a boiling-water bath. The solution when cool is taken up in 400 ml of benzene and worked up as described above for the alpha isomer. The crystals obtained after recrystallization from alcohol weigh about 140 g. Phenyl tetraacetyl-β-*d*-glucopyranoside melts at 124° to 125° C and gives $[\alpha]_D^{20} = -22.0°$ (chloroform).

(e) PREPARATION OF GLYCOSIDES FROM SUGAR MERCAPTALS

This method is particularly useful for preparing furanose glycosides [23], but it may also be used for obtaining the pyranose glycosides [24], the thiofuranosides, and the thiopyranosides. The method consists in treating the sugar mercaptal dissolved in the alcohol with mercuric chloride, and when furanosides are desired, mercuric oxide. The product formed depends upon the conditions employed. Thus the galactofuranosides are formed at room temperature and in neutral ethyl alcoholic solution in the presence of mercuric oxide. In a boiling solution containing hydrogen chloride (which is formed during the reaction) the ethyl α-*d*-galactopyranoside is produced in 90-percent yield. A water suspension of the galactose ethyl mercaptal, mercuric oxide, and mercuric chloride gives at 0° C the crystalline ethyl galactothiofuranoside.

(1) Ethyl *d*-galactofuranosides.

Method [25].—To a solution of 28 g of galactose ethyl mercaptal in 250 ml of absolute alcohol at 70° C, 35 g of yellow mercuric oxide and 10 g of powdered Drierite[1] are added. The mixture is stirred rapidly while a solution of 35 g of mercuric chloride in 150 ml of absolute ethyl alcohol is added over a period of 30 to 40 minutes. The reaction mixture is allowed to cool to 30° C over about an hour's

time. It is then filtered, 10 ml of pyridine is added to the filtrate, and the solution is allowed to stand at 0° C overnight. The pyridine-mercuric-chloride compound is separated by filtration; the filtrate is evaporated in vacuo to a sirup, which is dissolved in 100 ml of water, neutralized with dilute alkali (phenolphthalein indicator), and the solution again evaporated to a sirup. This sirup is dehydrated by several distillations with absolute alcohol, and finally a thick sirup is left. This is taken up with hot ethyl acetate, and the solution cooled and decanted from the sirupy phase which forms during the cooling. Seed of ethyl *β-d*-galactofuranoside[2] is added and crystallization is allowed to take place in a refrigerator. About 10 g of ethyl-*β-d*-galactofuranoside is obtained. The material, after recrystallization from 30 ml of hot ethyl acetate, melts at 85° to 86° C and gives $[\alpha]_D^{20}=-102°$ (water, $c=1$).

The mother liquor is concentrated in vacuo to a volume of 200 ml and crystallization is allowed to take place. The crystalline mixture of alpha and beta galactofuranosides may be mechanically separated since ethyl *β-d*-galactofuranoside crystallizes as white fragile needles, while ethyl *α-d*-galactofuranoside[2] separates as round translucent buttons which cling to the wall of the flask. The crude alpha isomer is purified by recrystallization from 100 times its weight of hot ethyl acetate from which it crystallizes in short needles. Ethyl *α-d*-galactofuranoside melts at 140° C and gives $[\alpha]_D^{20}=+92°$ (water, $c=1$).

NOTES

[1] Drierite is a trade name for an anhydrous calcium sulfate.
[2] Nomenclature as given in reference [25].

(2) Methyl *d*-Glucopyranosides.

Method [24].—Glucose dibenzyl mercaptal (8.2 g) is dissolved in 100 ml of boiling methyl alcohol and a solution of 16.3 g of mercuric chloride in 30 ml of warm methyl alcohol is added. After the solution has been heated for 15 minutes on the water bath, the precipitate of $C_6H_5-CH_2-S-HgCl$ is removed by a filtration. Dry hydrogen sulfide gas is passed into the solution and it is again filtered. The filtrate is neutralized with silver carbonate, treated with a decolorizing carbon, and filtered. The filtrate is evaporated in vacuo to a sirup, which is taken up in a little cold water and filtered to remove the insoluble portion. The aqueous solution is concentrated under reduced pressure to a heavy sirup, which is brought to crystallization by the addition of absolute alcohol. The product is separated and recrystallized from 18 parts of hot absolute alcohol. About 2.8 g of methyl *α-d*-glucopyranoside is obtained. It melts at 166° C and gives $[\alpha]_D^{20}=+158.9°$ (water, $c=10$).

The mother liquors from the preparation of the alpha isomer are allowed to stand in a refrigerator. After several days the resulting crystals of methyl *β-d*-glucopyranoside are separated and recrystallized from 8 parts of absolute alcohol. About 0.7 g of methyl *β-d*-glucopyranoside is obtained. The compound melts at 105° C and gives $[\alpha]_D^{20}=-34.2°$ (water, $c=10$).

(f) PREPARATION OF GLYCOSIDES FROM SUGARS WITH DIMETHYL SULFATE

By careful methylation with one equivalent of dimethyl sulfate, methyl glycosides may be obtained directly from the sugars [5, 26].

(1) Methyl β-*d*-Mannopyranoside Isopropyl Alcoholate.

Method[1] [5].—A solution of 18 g of mannose dissolved in 100 ml of water is kept in an ice bath and stirred while dimethyl sulfate and 30-percent sodium hydroxide are added dropwise over a period of 2 to 3 hours at such a rate as to maintain the reaction of the solution alkaline to acyl blue (pH 12). Fifteen milliliters of dimethyl sulfate is added over a period of 2 to 3 hours, and 20 to 22 ml of alkali in the course of 8 hours. After the solution has stood overnight at room temperature, it is neutralized with sulfuric acid and filtered. A small quantity of barium carbonate is added to the filtered solution, which is then concentrated in vacuo to a volume of approximately 30 ml. After the addition of 60 ml of dioxane and a second evaporation, the solution is concentrated to a thick sirup, which is dissolved in 60 ml of pyridine. The solution is filtered, mixed with an equal volume of acetic anhydride, and allowed to stand overnight at room temperature. It is then poured with stirring into a mixture of cracked ice and water, and the acetylated glycoside is extracted with chloroform. The chloroform solution is washed successively with solutions of sodium bicarbonate and copper sulfate (until free from pyridine), and finally with water. The chloroform solution is dried, filtered, and evaporated to a sirup which is brought to crystallization by the addition of ethyl alcohol and further concentration. The material is removed from the flask with ether (100 ml) and petroleum ether added to saturation. After the mixture stands for a day at 0° C, the crystals are collected on a filter and washed with a mixture of ether and petroleum ether. The yield of the mixed alpha and beta methyl tetraacetylmannosides is about 18 g. This material is stirred with 100 ml of ether and filtered. The insoluble portion, about 6 g, is nearly pure methyl tetraacetyl-β-*d*-mannopyranoside. The compound melts at 161° C and gives $[\alpha]_D^{20}=-50.4°$ (chloroform, $c=1$).

The acetylated glycoside is deacetylated by the barium methylate method described on page 493. After the barium is removed, the resulting solution is treated with a decolorizing carbon, filtered, and evaporated in vacuo to a heavy sirup, which is taken up in 10 ml of isopropyl alcohol. After the mixture has stood for a short time, methyl β-*d*-mannoside, containing isopropyl alcohol of crystallization ($C_7H_{14}O_6 \cdot C_3H_8O$) separates in large thin plates. The yield is nearly quantitative. Methyl β-*d*-mannopyranoside isopropyl alcoholate melts at 74° to 75° C and gives $[\alpha]_D^{20}=-53.3°$ (water, $c=4$).

NOTE

[1] The methylation described here is like that used by Schlubach and Maurer [26] for the preparation of β-methyl glucoside. The dimethyl sulfate method is particularly useful for the preparation of those glycosides in which the methoxyl and the hydroxyl on the adjacent carbon are *cis*, because such glycosides are not produced in satisfactory yield by the Koenigs-Knorr reaction. Methyl β-*d*-mannopyranoside may be prepared also by the hydrogen chloride method [27].

(g) PREPARATION OF GLYCOSIDES BY THE USE OF ALKYL IODIDES AND SILVER OXIDE

(1) Methyl Tetraacetyl-β-*d*-fructopyranoside.

Method [1] [28].—Sixty grams of powdered tetraacetylfructose, 375 g of freshly prepared silver oxide, and 340 ml of methyl iodide are boiled on the water bath for 6 hours in a 2-liter flask fitted with a

reflux condenser which is supplied with ice water in order to prevent loss of the solvent.[2] The methyl iodide is then distilled off and recovered.[3] The residue from the distillation is mixed with ether, and the solution filtered and evaporated in the air. On seeding the resulting colorless sirup, crystalline methyl tetraacetyl-β-*d*-fructopyranoside is obtained in almost the theoretical yield. The product, purified by recrystallization from petroleum ether, melts at 75° to 76° C and gives $[\alpha]_D^{20}=-124.6°$ (chloroform, $c=8$).

NOTES

[1] A general review of the methylation method is given in reference [29].

[2] The reaction can also be carried out at room temperature if the mixture is shaken and a longer reaction time is allowed.

[3] A large flask should be used for this evaporation in order to prevent loss by bumping.

(2) METHYL α-*d*-MANNOFURANOSIDE.

Method [30].—Four-tenths gram of 2,3–5,6-mannose dicarbonate is dissolved in methyl iodide containing a little acetone, and small amounts of silver oxide are added at intervals during a half hour, while the solution is heated below the boiling point. Prolonged contact with large excesses of silver oxide is harmful. The solution is filtered and the residue extracted with boiling acetone. The original filtrate and the acetone extracts are evaporated and the residue is again treated with the methylating agents as before. The filtrate from the second treatment yields on evaporation 0.15 g of methyl 2,3–5,6-α-*d*-mannofuranoside dicarbonate. This product separates in colorless crystals which are sparingly soluble in ethyl acetate and melt at 172° to 173° C with decomposition. The carbonate groups are removed by saponification with barium hydroxide. The relatively pure compound thus obtained crystallizes readily. Methyl α-*d*-mannofuranoside melts at 118° to 119° C and gives $[\alpha]_D^{20}=+113°$ (water, $c=1$).

Other methods for preparing glycosides.—A number of other methods of limited applicability have been used for the preparation of glycosides. Thus methyl α-*d*-glucoside has been obtained by enzymatic synthesis from aqueous methyl alcoholic solutions of glucose and α-glucosidase [31].

Certain glycosides can be prepared conveniently by the oxidation of glycals with perbenzoic acid in the presence of an alcohol. Methyl α-*d*-mannoside is prepared in good yield by this method from glucal [32].

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10. MERCAPTALS

(a) PREPARATION OF MERCAPTALS

These substances are thioacetal derivatives of the aldehydo forms of the sugars and are used for the preparation of acetylated aldehydo derivatives (see p. 490), for the preparation of pyranose and furanose glycosides (see p. 517), and for the isolation of sugars from impure mixtures. The mercaptals of a large number of sugars have been prepared by shaking the sugar with the mercaptan in the presence of concentrated hydrochloric acid at room temperature. The process is not applicable to disaccharides, as partial hydrolysis occurs. The detailed procedure for the preparation of galactose ethyl mercaptal given in this section is typical of the method in general.

(1) Galactose Ethyl Mercaptal.

Method. [1,2].—Fifty grams of galactose is placed in a 500-ml glass-stoppered wide-mouth bottle and is dissolved at room temperature in 75 ml of concentrated hydrochloric acid (sp. gr 1.19). Fifty ml of technical ethyl mercaptan is then added and the mixture is shaken, the pressure being released at intervals. After 5 minutes ice and water is added to the reaction mixture. The crystalline product which forms is separated by filtration and recrystallized, first from absolute alcohol and then from hot water. About 37 g of pure material is obtained which melts at 140° to 142° C.

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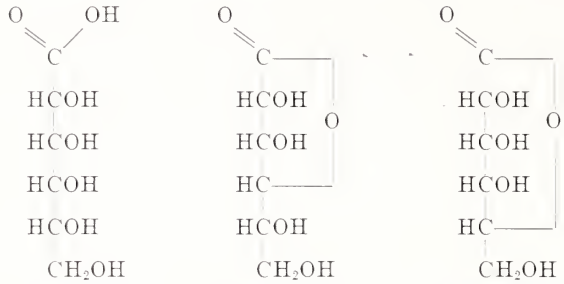
11. OXIDATION PRODUCTS

(a) PREPARATION OF ALDONIC ACIDS

General characteristics.—In aqueous solution the aldonic acids establish an equilibrium between the free acid (I), the gamma lactone (II), the delta lactone (III), and frequently condensation products.



(I) Aldonic acid. (II) Aldonic γ-lactone. (III) Aldonic δ-lactone.

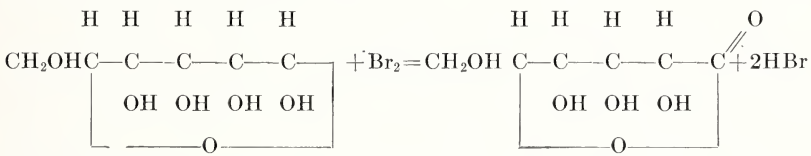
The relative proportions of the free acid and delta and gamma lactones vary greatly according to the configuration of the sugar acid and according to the temperature and concentration of the solution. To prepare the free acids, it is generally necessary to avoid lactone formation. Usually the crystalline acid can be obtained by concentrating a freshly prepared aqueous alcoholic solution of the acid at a low temperature as rapidly as possible. The use of isoamyl or butyl alcohol is advantageous because these alcohols retard the rate of lactone formation, facilitate removal of the water, and after partial evaporation, leave a solvent from which the acid crystallizes readily. The lactones, when pure, also crystallize readily, but frequently this condition cannot be realized experimentally because of the simultaneous formation of two lactones. If one dissolves mannonic acid in water, the delta lactone is formed more rapidly than the gamma lactone, but the two are formed simultaneously. After several hours the concentration of the delta lactone reaches a maximum and at this point it may be crystallized from the solution. As the solution stands, the concentration of the more slowly formed gamma lactone increases at the expense of the free acid and the delta lactone until equilibrium is reached, when nearly all the sugar acid may be present as the gamma lactone. The position of equilibrium depends on the experimental conditions and on the configuration of the acid. The equilibrium state for gluconic acid permits the crystallization of either the free acid or the delta lactone from the equilibrium solution. At temperatures below 25° C free gluconic acid is obtained, whereas at temperatures above 25° C the delta lactone crystallizes. Heating gluconic acid in a high-boiling solvent, such as butyl alcohol, results in the formation of gluconic γ-lactone, which crystallizes when the solution is cooled. The sugar acids combine with alcohols readily to form esters which sometimes interfere with the crystallization of the acids or lactones. Heating the esters in alcoholic solution, especially in the presence of a mineral acid, causes the formation of lactones. The ethyl ester of gluconic acid crystallizes well and decomposes on heating to give gluconic γ-lactone. Lactone formation is accelerated by acid catalysts; consequently, if one wishes to prepare the free acid, the presence of mineral acid is avoided, but if one wishes to establish the equilibrium state quickly, as in the preparation of mannonic γ-lactone, a mineral acid is added.

The aldonic acids may be prepared from the aldoses with the same number of carbon atoms by oxidation, from the ketoses with more

carbon atoms by degradation, or from either the aldoses or the ketoses with fewer carbon atoms by means of the cyanhydrin reaction.

Certain acids may be prepared by mold fermentation [1]. Many oxidizing agents have been used for oxidizing aldoses to sugar acids, among which may be mentioned bromine [2], iodine [3], mercuric oxide [4], and chlorine in the presence of bromides or iodides [5]. One of the best methods for the manufacture of the aldonic acids is the electrolytic process of Isbell and Frush [6, 7]. The electrolysis is conducted in the presence of a bromide so that the real oxidant is bromine set free by electrolysis. Presumably the bromine reacts with the sugar, forming the aldonic acid and hydrogen bromide. If the reaction is conducted in the presence of calcium bromide and calcium carbonate, the sugar acid and hydrogen bromide combine with the calcium carbonate, regenerating the calcium bromide and forming the calcium salt of the sugar acid. Inasmuch as only a small quantity of bromide is used as a catalyst in the electrolytic process, it is ordinarily not necessary to remove it after the oxidation is complete. The method used for the preparation of calcium gluconate, described on page 524, can be used for the preparation of any alkaline earth salt of the sugar acids.

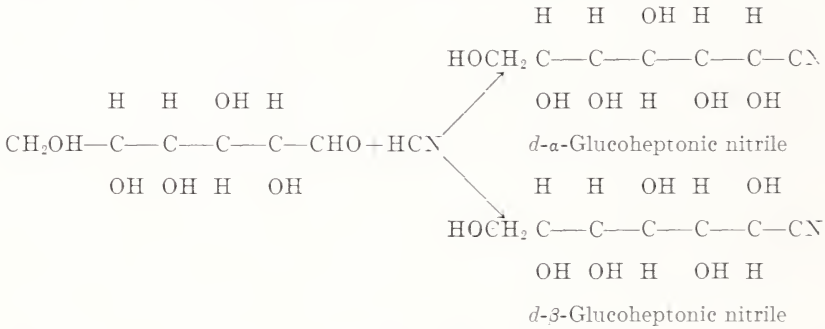
Bromine reacts with the aldoses in either acid or alkaline solution, whereas iodine reacts only in alkaline solution. In the bromine oxidation the active oxidant in the acid solution is *free* bromine [8], but in the alkaline solution the active oxidant is hypobromite. In acid solution the ring modifications of the sugar appear to be converted directly to the lactone [9], while in alkaline solution the open-chain and enolic modifications appear to be oxidized. As shown by the following equation, 2 moles of hydrobromic acid are formed by oxidation of 1 mole of the sugar:



The hydrobromic acid which is formed greatly reduces the rate of reaction, but the retarding effect can be overcome by the addition of a neutralizing agent. Usually, calcium or barium carbonate is suitable for this purpose, but if one wishes to oxidize aldoses in the presence of ketoses without damaging the latter, the oxidation should be conducted in the presence of barium benzoate [10]. The hydrobromic acid or the bromide formed as a byproduct of the oxidation is ordinarily removed with silver or lead carbonate. If the oxidation is conducted in the presence of calcium or barium carbonate, it is advisable to remove the calcium or barium first with sulfuric acid, and then to remove the hydrobromic acid with silver carbonate.

Aldonic acids containing fewer carbon atoms than the parent sugars may be obtained by oxidizing the sugars with gaseous oxygen in alkaline solution [11, 12]. This method is satisfactory for either aldoses or ketoses and may be used for identification purposes. The preparation of potassium *d*-arabonate from levulose given on page 528 illustrates the method. The same substance is easily obtained from *d*-glucose.

Aldonic acids containing more carbon atoms than the parent sugar are usually prepared by the cyanhydrin synthesis. Cyanides react with the reducing sugars, forming nitriles which on saponification yield acid amides that on further hydrolysis give the aldonic acids [13]. The reaction may be brought about either by hydrogen cyanide in the presence of ammonia or by a metallic cyanide. Perhaps the most convenient reagent is a mixture of sodium cyanide and calcium chloride [14]. A solution of the sugar is mixed with a solution containing an equivalent quantity of the cyanide, and after time has been allowed for the addition reaction to take place, the resulting nitriles are hydrolyzed with alkali or with acid. If alkaline hydrolysis is employed, the product is conveniently separated in the form of basic calcium salts [15]. If acid hydrolysis is used, the product can be obtained directly in the form of the lactone. As may be seen from the following equation, the addition of hydrogen cyanide to the aldose results in the formation of the nitriles of two epimeric acids. These acids differ merely in the configuration of the second carbon, and the separation of the two is frequently a difficult process.



The following methods may be employed for the purification and separation of aldonic acids: (1) Precipitation as basic calcium salts, followed by conversion to normal salts and their fractional crystallization [15]; (2) separation of the acid as the amide [16]; (3) hydrolysis of the nitriles to the free acids and separation of the products, as the crystalline acids or as lactones [17, 18]; (4) formation of double salts [19, 20]; (5) formation of benzal compounds [21]; (6) formation of phenylhydrazides [16]; (7) separation by means of lead [22], strontium [23], magnesium [24], cadmium [25], potassium [11], strychnine [26], or brucine salts [27].

If the raw material for the preparation of the sugar acids by one of the methods already given is not available, the sugar acid can be made from another sugar acid by the inversion of the asymmetric center on the second carbon (epimerization). This can be accomplished by heating the acid or lactone with pyridine, quinoline, or aqueous barium hydroxide. The preparation of talonic acid from galactonic acid, given on page 528, is a typical example of this method.

(1) Preparation of Calcium Gluconate by Electrolytic Oxidation.[1]

Method [6, 7, 28].—A solution consisting of 45 g (0.25 mole) of anhydrous dextrose and 8 g of calcium bromide in sufficient water to make 1 liter is placed with 12.5 g of calcium carbonate in a 2-liter three-necked flask. The flask is equipped with a mechanical stirrer

and two graphite electrodes 22 mm in diameter and sufficiently long to reach the bottom of the flask.[2] The electrodes are connected with a source of direct current at 5 to 10 volts. A current of 0.5 ampere is passed through the solution and the quantity of electricity is measured. The amount of oxidation is nearly proportional to the quantity of electricity used, and the oxidation is virtually complete when the theoretical amount (13.4 ampere hours) has passed through the solution.[3,4] The current is interrupted when a quantitative test for reducing sugars shows that substantially all the sugar has been used. The electrolyzed solution is filtered and concentrated in vacuo to a thin sirup from which calcium gluconate crystallizes readily. The crystalline salt is separated, and if desired, the mother liquors may be returned to the electrolytic cell and after the addition of more sugar and calcium carbonate the process may be repeated. The yield of calcium gluconate obtained in a single run is about 45 g. The crude salt is recrystallized by dissolving it in hot water and permitting crystallization to take place while the solution is stirred and cooled.

NOTES

[1] Licenses under United States Patent 1,976,731 covering the electrolytic process for the manufacture of calcium gluconate and other sugar acids may be applied for from the Secretary of Commerce.

[2] Impregnating the electrodes with paraffin prolongs their life.

[3] Each mole of sugar requires 2 faradays (53.6 ampere hours).

[4] Sometimes a calcareous deposit forms on the electrodes which may be removed by reversing the current.

(2) Preparation of Calcium Lactobionate-Calcium Bromide.—The method for the preparation of calcium lactobionate-calcium bromide is essentially the same as that used for the manufacture of calcium gluconate, except that one equivalent of bromine is added in place of the calcium bromide and 1 faraday of electricity is used for each mole of lactose. If desired, the electrolytic cell can be operated in a continuous manner, in which case lactose, calcium carbonate, and bromine are added, while calcium lactobionate-calcium bromide is crystallized from the electrolyzed solution. In small-scale operations, it is generally more convenient to add the lactose, bromine, and calcium carbonate in batches rather than continuously and to separate the product from time to time. To avoid the handling of bromine, the process can be conducted by adding calcium bromide in place of bromine and by using 2 faradays of electricity per mole of lactose. The following procedure has been found to give satisfactory results:

Method [1] [20].—One kilogram of precipitated calcium carbonate and 3.6 kg of lactose dissolved in 10 liters of water are placed in a 20-liter crock equipped with a mechanical stirrer and eight graphite electrodes 30 cm long and 2.3 cm in diameter. While the solution is stirred vigorously, 0.8 kg of bromine is cautiously added. Considerable foaming occurs which can be controlled by adding a few milliliters of an antifoam agent such as normal hexyl alcohol. After the bromine has been added, and the evolution of carbon dioxide has subsided, a direct current is passed through the solution, using alternate electrodes as anodes and cathodes. The current density should be from 1 to 2 amperes per square decimeter of anode surface. This requires about 6 volts. After about 280 ampere-hours, when

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substantially all the sugar has been oxidized, the electric current is stopped but stirring is continued until the evolution of carbon dioxide ceases. After filtration the electrolyzed solution is concentrated under reduced pressure to a sirup, from which nearly pure calcium lactobionate-calcium bromide crystallizes. The crystals can be grown in the evaporating pan while concentration is taking place. The resulting crystalline product is separated from the mother liquor by

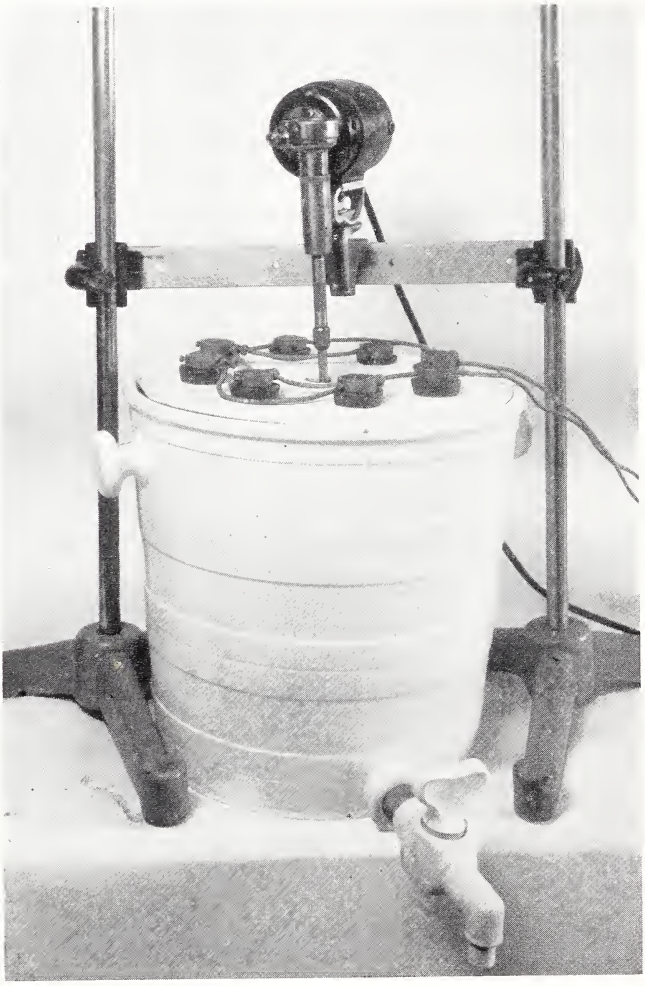

FIGURE 114.—*Apparatus for the electrolytic oxidation of sugars.*

means of a centrifugal machine and washed with a high-purity calcium-lactobionate-calcium-bromide sirup. The mother liquors are ordinarily returned to the electrolytic cell and worked up with the following batch. Yields of over 90 percent are obtained.

Recrystallization.—Three parts of the salt are dissolved in 2 parts of boiling water. A small quantity of a decolorizing carbon is added and the hot solution is filtered. The filtrate is seeded with powdered

crystalline calcium lactobionate-calcium bromide and allowed to cool while kept in constant agitation. The crystals are collected on a filter and washed, first with a small quantity of water saturated with calcium lactobionate-calcium bromide and finally with aqueous alcohol containing approximately equal volumes of alcohol and water. The The product, after drying at 50°C, corresponds to the formula: $Ca(C_{12}H_{21}O_{12})_2.CaBr_2.6H_2O$. It contains 7.54 percent of calcium and 15.04 percent of bromine and gives $[\alpha]_D^{20}=+18.7°$ (water, $c=7.3$). A saturated solution of the hydrated salt at 20°C contains 31.5 percent by weight and has a density of 1.18 g per milliliter.

NOTES

[1] Those desiring to use this process for the manufacture of calcium lactobionate-calcium bromide may apply for a license from the Secretary of Commerce under United States Patent No. 1,976,731 and No. 2,186,975. The compound has been introduced into the pharmaceutical trade under the name Ca-Br-Galactogluconate.

(3) Preparation of Calcium Altronate and Allonic Lactone by the Cyanhydrin Synthesis.

Method [29, 30].—The following solutions are prepared: 50 g of *d*-ribose in 500 ml of water; 18 g of sodium cyanide in 100 ml of water; 27 g of $CaCl_2.2H_2O$ in 100 ml of water.

The sugar, cyanide, and calcium chloride solutions are mixed and allowed to stand overnight. Then there is added slowly, in portions, with vigorous stirring, 74 g of calcium hydroxide in 500 ml of water. The solution is heated to 80° C and allowed to stand overnight or until saponification is complete. The solution is again heated to about 80° C and filtered while hot. The precipitate of basic calcium salts is washed with lime water until the filtrate shows only a faint test for chlorides.

The precipitate of basic calcium altronate and basic calcium allonate is suspended in water and dilute oxalic acid is added until the solution is neutral.[1] The calcium oxalate is separated by filtration and washed with hot water. The filtrate contains calcium altronate and calcium allonate. The solution is boiled down in vacuo to a thin sirup (about a 20-percent solution) and alcohol is added until a slightly opalescent mixture results. On standing, calcium altronate crystallizes from the solution. The mixture is then allowed to stand for several days in order to separate all the calcium altronate possible at this point. Sufficient oxalic acid is added to the mother liquors to remove the calcium. The solution, after removal of the calcium oxalate, is evaporated to a sirup, from which crystalline allonic lactone separates. The lactone is purified by recrystallization from water.

A small quantity of calcium altronate and a little allonic lactone can be reclaimed from the mother liquors by converting them to the calcium salts, separating the calcium altronate and allonic lactone as before. The average yield from 50 g of ribose is about 25 g of calcium altronate and 25 g of allonic lactone.

NOTE

[1] In place of oxalic acid, sulfuric acid or carbon dioxide may be used.

(4) Preparation of *d*-Talonic Acid by Pyridine Rearrangement of Galactonic Acid.

Method [25, 31].—Talonic acid is prepared from *d*-galactonic acid by epimerization with pyridine. Eighty grams of *d*-galactonic lactone monohydrate, 36 g of pyridine, and 500 ml of water are placed in a 1-liter flask and heated at 90° to 100° C for 115 hours. The solution is then evaporated to about 100 ml under reduced pressure. The residue in the flask is mixed with 25 g of cadmium carbonate and 1 liter of water. The resulting suspension is then boiled while the volume is kept constant until nearly all the carbonate is dissolved. The solution is then concentrated under reduced pressure to remove the pyridine. The resulting sirup is diluted to 1 liter with water and after treatment with a decolorizing carbon and boiling to dissolve all cadmium galactonate, the hot solution is filtered. Fifteen grams of cadmium hydroxide is added to the filtrate and the solution is boiled for some time, filtered hot, and evaporated to about 400 ml, after which it is allowed to stand overnight. The crystalline cadmium galactonate which separates is removed by filtration and the filtrate concentrated to about 100 ml and allowed to stand overnight. Cadmium galactonate which separates is removed again by filtration. The filtrate is then evaporated to dryness and taken up in 100 ml of water. The cadmium is removed by treating with hydrogen sulfide to precipitate the metal. An excess of hydrogen sulfide is avoided because it makes the filtration difficult. The precipitated cadmium sulfide is separated by filtration and the filtrate is concentrated almost to dryness under reduced pressure at a temperature of not more than 50° C. The residue in the flask is mixed with 500 ml of absolute alcohol and allowed to stand in the ice box overnight. About 20 g of crystalline talonic acid separates.

Recrystallization.—The crude talonic acid is dissolved in the least possible quantity of water at 40° C. The solution is cooled and poured into 5 volumes of absolute alcohol. After standing for several hours in the refrigerator, the resulting crystals are separated. Pure *d*-talonic acid melts at 138° C and gives $[\alpha]_D^{20}=+19°$ (water, $c=4$).

(5) Preparation of Potassium *d*-Arabonate from Levulose by Oxidation in Alkaline Solution.

Method [11].—A solution of 18 g (0.1 mole) of levulose in 150 ml of water is added to 150 ml of 2 *N* potassium hydroxide in a flask equipped with a mechanical stirrer and a tube for the introduction of oxygen. The air in the system is displaced by oxygen and oxidation is allowed to take place at about 20° C. Stirring is continued for about 1 day. Then the reaction mixture is concentrated to a thin sirup, which is diluted with 750 ml of methyl alcohol to precipitate the potassium salt of the sugar acid. The alcoholic solution containing the excess potassium hydroxide is decanted. The oily precipitate is dissolved in water, and the solution is clarified with a decolorizing carbon and evaporated. Crystals of potassium *d*-arabonate form during the evaporation and are separated by filtration. The yield is about 70 percent.

(b) PREPARATION OF DIBASIC ACIDS

(1) Preparation of Mucic Acid by the Oxidation of Galactose with Nitric Acid.

Method [32].—Five grams of galactose is treated with 60 ml of nitric acid of 1.15 specific gravity (about 25 percent) and heated on a steam

bath with occasional stirring until the volume has diminished to one-third. The following day the product is stirred with 10 ml of water, and after 24 hours the crystallized mucic acid is separated and washed with 25 ml of water. The product is recrystallized from hot water. The method can be used for the quantitative estimation of galactose or galactose-containing substances.

(c) PERIODIC ACID OXIDATION OF GLYCOSIDES

Periodic acid oxidation of the methyl glycosides according to the method of Jackson and Hudson [33] provides a convenient means for the determination of ring structure and the configuration of the glycosidic carbon. For an unknown substance it is merely necessary to follow the rotatory change during oxidation and determine the unused periodic acid by titration. In the oxidation, the alpha and beta methyl pentapyranosides form *D'*- or *L'*-methoxy-diglycolic aldehydes, giving $[\alpha]_D^{20}$=approximately $\pm 124°$. The alpha and beta methyl hexapyranosides and pentafuranosides of the *d* series form *D'*- or *L'*-methoxy-*D*-hydroxymethyl-diglycolic aldehydes which give $[\alpha]_D^{20}$=about $+120°$ and $-150°$, respectively. The specific rotation after oxidation indicates the configuration of the glycosidic carbon, while the amount of periodic acid used indicates the ring structure. Oxidation of a pentapyranoside or hexapyranoside requires 2 moles of periodic acid, while oxidation of a furanoside requires 1 mole.

Method [33].—A known weight of the glycoside (approximately 2 g of the pentoside or 2.4 g of the hexoside) is dissolved in 98 ml of a standardized solution of periodic acid (about 0.3 *M*) in a 100-ml volumetric flask at 20°C. The rotatory change is followed at 20°C until the rotation becomes constant.[1] The excess periodic acid is then determined as follows [34]: A sample of the solution of suitable size is treated with 5 to 10 ml of a saturated solution of sodium bicarbonate, 15 ml of 0.1 *N* carbonated arsenious acid, and 1 ml of 20-percent potassium iodide. After standing for 15 minutes at room temperature, the excess arsenious acid is titrated with 0.1 *N* iodine solution.

NOTE

[1] For the subsequent oxidation to the diglycolic acids, isolation of the strontium or barium salts and hydrolysis, see Jackson and Hudson [33].

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12. REDUCTION PRODUCTS

(a) ALCOHOLS

General characteristics.—The sugar alcohols may be prepared by reduction of the sugars and sugar acids with sodium amalgam, by catalytic reduction of the sugars with hydrogen, or by electrolytic reduction of the sugars. Electrolytic reduction of sugars has been developed commercially under the patents of Creighton [1, 2]. The reaction is carried out by cathodic reduction of the sugar, using lead electrodes and sodium sulfate as electrolyte. Sorbitol and mannitol are obtained from dextrose by this process. The catalytic reduction of the sugars to polyhydric alcohols with hydrogen was reported by Ipatieff in 1912 [3]. Glucose was reduced to sorbitol, fructose to mannitol (and presumably sorbitol), while lactose was split and reduced to dulcitol (and presumably sorbitol). Senderens [4] studied the high-pressure hydrogenation of lactose further, and obtained a crystalline lactositol hydrate from the sirupy mother liquor after removal of the dulcitol. Böeseken and Leefers [5] used a nickel and cobalt catalyst and hydrogenated glucose in 95-percent alcohol. Nickel catalysts, such as Raney nickel [6] are generally used in sugar hydrogenation [7, 8, 9].

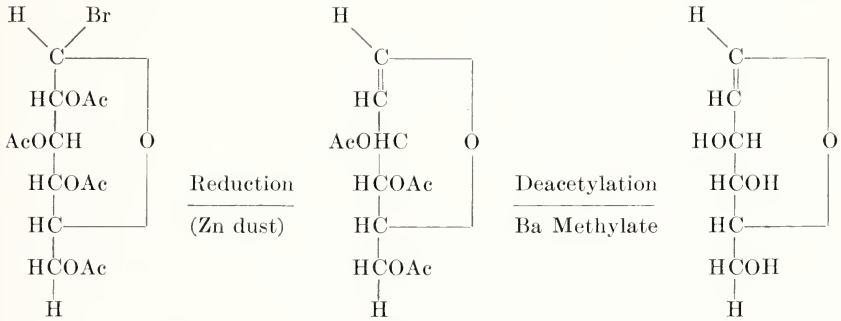
(1) Reduction of *d*-α-Glucoheptose With Sodium Amalgam to Give *d*-α-Glucoheptitol.

Method [10].—Ten grams of *d*-α-glucoheptose is dissolved in 100 ml of water at room temperature, and after addition of 4 ml of 20-percent sulfuric acid, 300 g of pure 2.5-percent sodium amalgam is introduced. The mixture must be continuously shaken and the reaction of the solution must be held slightly acid or neutral by the frequent addition of dilute sulfuric acid. When the sodium amalgam is spent, the mercury is separated and if the solution gives a positive test for reducing sugar, 200 g of sodium amalgam is added and the process is repeated while the reaction is held neutral to slightly alkaline. When the reduction is complete, as shown by a negative test for reducing sugars with Fehling solution, the aqueous liquid is decanted from the

mercury, neutralized with sulfuric acid, treated with a small quantity of a decolorizing carbon, and filtered. The filtrate is diluted five-fold with warm alcohol, filtered after cooling, and evaporated in vacuo to a sirup. After cooling and standing, the sirup yields crystalline *d*-α-glucoheptitol almost quantitatively. The crystalline mixture is triturated with alcohol, filtered, and recrystallized from ethyl or methyl alcohol. Pure *d*-α-glucoheptitol melts at 127° to 128° C and is optically inactive.

(b) GLYCALS

General characteristics.—The glycals are unsaturated derivatives containing two hydroxyls less than the parent sugars. Usually they are prepared by the reactions represented by the following equations:

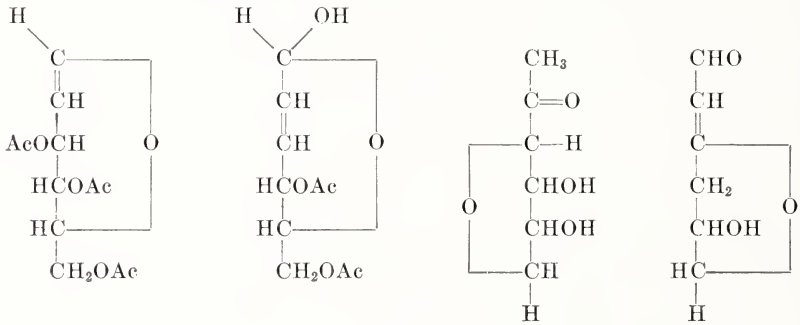


1-Bromo-2,3,4,6-tetraacetyl-α-*d*-glucose. Triacetylglucal. Glucal.

The glycals are of importance because they can be used for the preparation of new sugars and sugar derivatives. Oxidation of glycals with perbenzoic acid followed by treatment with water gives a mixture of the two epimeric sugars [11]; hence, by conversion of a sugar into its glycal and subsequent oxidation, the epimeric sugar may be prepared. Strangely, substitution of the hydroxyls greatly alters the proportions of the epimeric sugars produced. Thus the oxidation of triacetylglucal gives almost exclusively glucose derivatives, whereas the oxidation of glucal gives glucose and mannose, with mannose in predominating quantity [11, 12]. By treating glycals with perbenzoic acid in the absence of water, followed by the addition of methyl alcohol, methyl glycosides are obtained [11]. The products obtained by the perbenzoic acid oxidation usually contain small quantities of monobenzoyl derivatives [13].

Treatment of the glycals with cold aqueous sulfuric acid gives sulfuric esters which on hydrolysis yield desoxy sugars. Chlorine adds to the double bond to give a mixture of epimeric 1,2-dichloro derivatives, while hydrobromic acid appears to give 2-bromo derivatives [14]. Oxidation of the glycals with ozone splits the molecule at the double bond. Reduction with hydrogen in the presence of a catalyst yields hydroglycals [14]. The behavior of the glycals towards hydrogen chloride provides a convenient qualitative test: A pine splinter moistened with a glycal solution and exposed to hydrogen chloride gas turns green.

The tendency of the glycals to undergo intramolecular change is particularly noteworthy and should be kept in mind when working with these products. Boiling triacetylglucal with water results in the migration of the double bond to the 2,3 position and the hydrolysis of one acetyl group [15]. The product, diacetylpseudoglucal, on treatment with barium hydroxide, undergoes further rearrangement to give isoglucal and protoglucal [16].



Triacetylglucal | Diacetyl-pseudoglucal | Isoglucal | Protoglucal

(1) Triacetylgalactal and Galactal.

Method [13].—To a 12-liter flask surrounded by an ice-salt bath there is added 1,000 ml of water, 500 ml of acetic acid, and 100 g of zinc dust which is kept in suspension by the aid of a mechanical stirrer. During a period of 3 hours, ten 75-g portions of finely powdered bromotetraacetylgalactose, each dissolved in 300 ml of warm glacial acetic acid, are added. Water is added in quantities to keep the composition at approximately 50-percent acid, and 600 g of zinc dust is added in portions at intervals during this period. The temperature is allowed to rise slowly to room temperature over a period of 18 hours. Then the mixture is filtered,[1] and the filtrate is extracted four times with a total of about 11 liters of benzene. The washed extracts are evaporated at a pressure of 14 mm to a thick sirup. The weight of the sirup, obtained by the combination of two such preparations from a total of 1,370 g of the bromo-tetraacetylgalactose, is about 685 g. This sirup is then purified by distillation at 140° to 155° C at a pressure of approximately 0.05 mm. The distillate (500 g) is deacetylated by dissolving it in 4 liters of dry methyl alcohol containing 0.1 mole of barium methylate.[2] After standing for 18 hours in the refrigerator, the solution is saturated with carbon dioxide and the barium carbonate is separated and discarded. The alcoholic solution is evaporated in vacuo to a thick sirup, which is dissolved in 200 ml of absolute alcohol and evaporated again. The resulting sirup is extracted with absolute ethyl alcohol. The insoluble residue is discarded and the extracts are concentrated to a sirup containing about 60 percent of solids. The galactal crystallizes readily from this solution. It is separated by filtration and recrystallized from hot ethyl acetate. About 200 g of the recrystallized product is obtained from 500 g of the acetate. The pure substance melts at 100° C.

NOTES

[1] Care must be taken to avoid oxidation of the zinc dust, which takes place when air is sucked through the residue on the filter.

[2] Sufficient barium methylate must be used to neutralize any acid present in the distillate and to leave an excess. This can be ascertained by diluting a small sample with water and adding phenolphthalein. An excess is indicated by a red color.

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XXXII. CRYSTALLOGRAPHY OF THE SUGARS

1. INTRODUCTION

All the sugars, being optically active, crystallize in one or another of the 11 enantiomorphous crystal classes. An enantiomorphous crystal is one which by reflection in a plane mirror yields an image like the object, but laterally inverted, and which cannot be made by rotation to resemble the first precisely, but behaves as a left hand does to a right hand. Both varieties of the crystals are known in many cases, familiar examples of which are right and left quartz and right and left tartaric acid. Also both right and left forms of many of the sugars have been prepared. By far the greater number of these fall into two crystal groups: Class 4, which has only one symmetry element, namely an axis of twofold or digonal symmetry; and class 6, which has three digonal symmetry axes intersecting each other at 90°. Class 4 is the only enantiomorphous class in the monoclinic system, and class 6 is the only one in the rhombic or orthorhombic system. These two classes only will be reviewed.

2. CHARACTERISTICS OF SYMMETRY CLASS 4 (MONOCLINIC SPHENOIDAL)

The monoclinic or monosymmetric system is characterized by three axes of unequal length, two of which, a and c, are inclined to each other, but the third, b, is perpendicular to those two. This may be written

$$a:b:c=?:1:? \qquad \alpha=\gamma=90,\ \beta=?$$

Class 4 of this system is characterized by the fact that there are no planes of symmetry and that only one of the three axes is an axis of

symmetry, namely the *b* axis. Half of a complete revolution about this axis restores the original appearance of the crystal. (See fig. 115, where the heavy dots represent crystal faces and the ellipse represents the digonal axis of symmetry.) It is known as the sphenoidal class, or digonal polar type, since the two ends of the *b* axis are of different crystallographic forms.

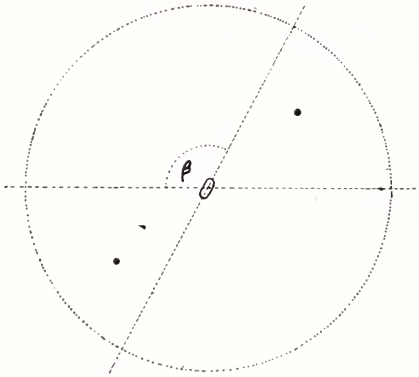

FIGURE 115.—*Symmetry elements of class 4.*

Table 63 shows the possible crystal forms of this class. Column 1 gives the form symbol; column 2, the Millerian index representing the form; column 3, the number of faces which comprise the form; and column 4, the name of the geometrical figure which the form comprises. In class 4 belong: Sucrose, α-dextrose hydrate, *d*-rhamnose monohydrate, α-lactose, and stachyose.

TABLE 63.—*Crystal forms of class 4*

Possible forms			
Form symbol	Millerian index	Number of faces	Name of geometrical figure which the form comprises
c	{001}	2	Basal pinacoid or third-order pinacoid.
a	{100}	2	Ortho-pinacoid or first-order pinacoid.
b	{010}	1	Right clino-pedion or right second pedion.
b'	$\{0\bar{1}0\}$	1	Left clino-pedion or left second pedion.
p	{*hk*0} {110}	2	Right monoclinic prism or sphenoid of third order.
p'	$\{h\bar{k}0\}$ $\{1\bar{1}0\}$	2	Left monoclinic prism or sphenoid of third order.
r	{*h*0*l*} {101}	2	Negative hemi-ortho-prism or negative pinacoid of second order.
r'	$\{h0\bar{l}\}$ $\{10\bar{1}\}$	2	Positive hemi-ortho-prism or positive pinacoid of second order.
q	{0*kl*} {011}	2	Right clino-prism or clino-dome, or right sphenoid of first order.
q'	$\{0\bar{k}l\}$ $\{0\bar{1}1\}$	2	Left clino-prism or clino-dome, or left sphenoid of first order.
o	{*hkl*} {111}	2	Right negative monoclinic sphenoid of the fourth order.
o'	$\{h\bar{k}l\}$ $\{1\bar{1}1\}$	2	Left negative monoclinic sphenoid of the fourth order.
o''	$\{\bar{h}kl\}$ $\{\bar{1}11\}$	2	Right positive monoclinic sphenoid of the fourth order.
o'''	$\{\bar{h}\bar{k}l\}$ $\{\bar{1}\bar{1}1\}$	2	Left positive monoclinic sphenoid of the fourth order.

(a) SUCROSE

Crystal system: Monoclinic.
Class 4: Monoclinic sphenoidal; monoclinic hemimorphic.
Symmetry type: Digonal polar, characterized by one digonal axis only.
Habit: Prismatic.
Ratio of axes: $a:b:c=1.2595:1:0.8782$.
$\beta=103°30'$ (Wolff) [3].

TABLE 64.—*Crystal forms of sucrose*

Possible forms	Usual forms observed
Crystal forms of class 4, see p. 534.	$a\{100\}$ $c\{001\}$ $r'\{10\bar{1}\}$ $p\{110\}$ $p'\{\bar{1}\bar{1}0\}$ $q\{0\bar{1}1\}$ $o\{\bar{1}\bar{1}1\}$ $r\{101\}$

TABLE 65.—*Angular values between faces of sucrose crystals*

Face form letter	Millerian face symbol	Calculated [1]	Hankel [1] 1840	Miller [2] 1842	Wolff [3] 1843	Rammelsberg [4] 1855	Rinne [5] 1885	Phelps [6] 1931	Vavrinecz [7] 1925
a–c	(100)–(001)	*76°30′*	76°30′	75°30′	76°30′	76°43′	76°15′	76°25′	77°5′
a–r	(100)–(101)	46°15′				45°37′		44°41′	45°11′
a–r	(100)–(101)	64°30′	63°45′	63°20′		64°27′	63°12′	63°32′	63°14′
a–p	(100)–(110)	50°48′	50°00′			50°46′	50°40′	50°44′	
c–r	(001)–(101)	30°15′				31°20′		31°42′	31°50
c–r	(001)–(101)	*39°00′*	39°45′	41°10′	39°00′	39°17′		40°00′	39°45′
c–q	(001)–(011)	40°30′						40°19′	41°5′
p–p	(110)–(110)	*78°28′*	80°00′	79°20′	78°28′	78°30′	78°48′	78°43′	78°41′
p′–p′	(110)–(110)	78°28′						78°53′	
q–q	(011)–(011)	99°00′						98°00′	
o–o	(111)–(111)	115°12′						114°30′	
o–r	(111)–(101)	32°24′						32°52′	
p–c	(110)–(001)								81°27′
o′–c	(111)–(001)								43°53′
p–a	(210)–(100)								31°11′
p_2–*p*	(210)–(110)								19°26′
p_3–*a*	(320)–(100)								40°13′
p_3–*p*	(320)–(110)								10°22′
p_5–*a*	(530)–(100)								36°10′
p_5–*p*	(530)–(110)								14°1′
p_4–*a*	(410)–(100)								16°30′
p_4–*p*	(410)–(110)								33°30′

[1] Calculated from the three italicized angles measured by Wolff.

Twinning: Frequent on the *c* axis.
Axial plane: $b\{010\}$
Cleavage: Along $a\{100\}$.
Solubility: Greater rate of solution on one end than on the other.
Double refraction: Negative.

$$\alpha=1.537,\ \beta=1.565,\ \gamma=1.571.$$

Refractive indices.—The optical ellipsoid is a surface representing the refractive index whose major, intermediate, and minor axes are determined by the maximum, intermediate, and minimum refractive indices of the crystal. The position of the optical ellipsoid with respect to the reference axes is determined in part by the crystal symmetry. For sucrose the axis of the optical ellipsoid which coincides with the symmetry or *b* reference axis of the crystal happens to be the intermediate axis; hence, the maximum and minimum axes, and conse-

quently the two optic axes of the crystal, lie in the plane of the stereographic projection.

Becke [8] found that the median line which coincides with one of the axes of the optical ellipsoid made an angle of 66°37′ with the crystallographic *c* axis in the obtuse angle β (sodium light), as shown in the stereographic projection (fig. 116). This value varies by about 6° from one end of the spectrum to the other, i. e., the position of the optical ellipsoid varies somewhat with the wave length of the light used to measure it.

Becke [8] measured the angle between the optic axes for sodium light and found it to be 48°0′ (fig. 116). By calculation from the measured refractive indices along the three principal directions of the ellipsoid, he obtained the value 48°22′.

Merwin [9] has redetermined the three principal refractive indices over a more extended range of wave lengths, as shown in table 66.

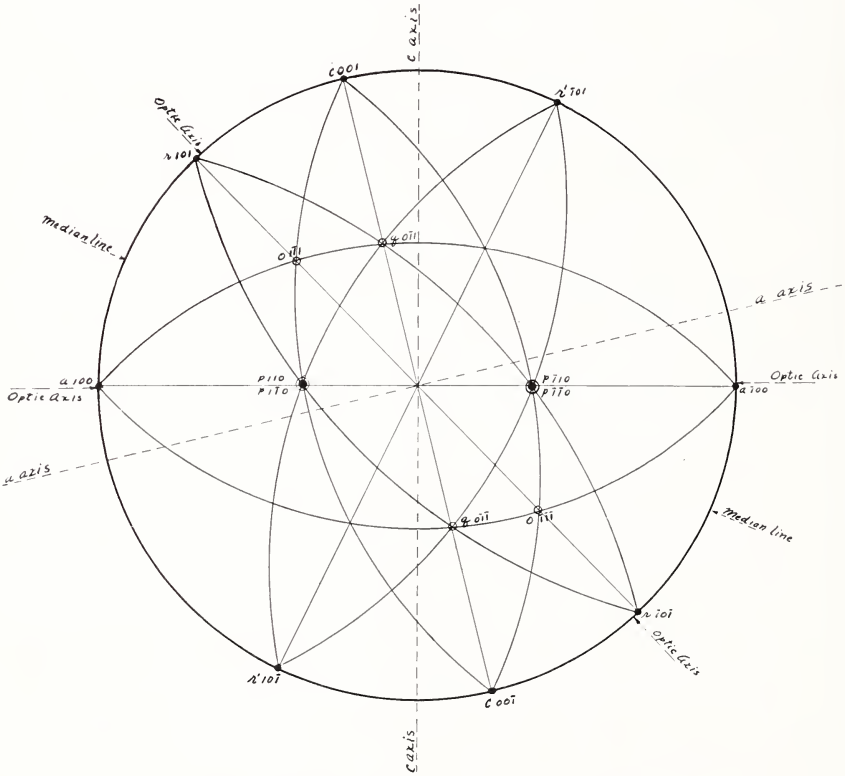

FIGURE 116.—*Stereographic net for sucrose.*

TABLE 66.—*Refractive indices of crystalline sucrose* [9]

λ	α	β	γ
Mμ			
405 Hg	1.5524	1.5803	1.5858
436 Hg	1.5484	1.5762	1.5816
502 He	1.5425	1.5702	1.5756
546 Hg	1.5397	1.5673	1.5727
588 He	1.5377	1.5652	1.5706
706 He	1.5336	1.5610	1.5664

It will be noted from the stereographic projection (fig. 116) that one of the optic axes is almost exactly perpendicular to the *a* faces and the other is approximately perpendicualr to the *r* faces. Along these two axial directions, sucrose in the crystalline state rotates the plane of polarization. The most recent study of this interesting phenomenon has been made by Longchambon [10] who gives $-15.6°$ per centimeter as the rotation along the axis nearly perpendicular to the *a* (100) faces, and $+51°$ per centimeter along the other optic axis, the rotation being of opposite sign along the two directions. Other investigators have given somewhat larger values. The cohesive forces tending to bind the units of the crystal together are least along the direction perpendicular to the *a* faces, as evidenced by the fact that the crystal cleaves easily into sections parallel to the *a* faces. This perhaps accounts for the usual prominent development of these faces.

Stammer [11], Schaaf [12], Bock [13], and Wulf [14] have studied

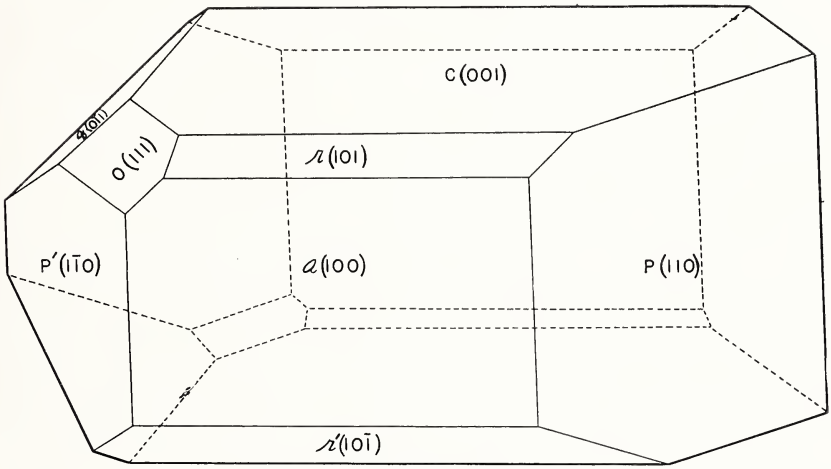

FIGURE 117.—*Sucrose crystal.*

the effects of various impurities upon the form or relative development of faces of sucrose crystals.

Their results may be summarized as follows: For pure sugar the faces shown on quickly grown crystals are *p*, *a*, *c*, and *r′* of somewhat near equal development (fig. 117 and fig. 118a). On more slowly grown crystals, the faces *r*, *q*, and *o′* are also usually developed, the latter two on the left end, as shown in figure 117. On crystals that have been rounded by filing and by solution, there frequently develop the following faces in addition to those above: On the left end, *b*, *o*, and 2*p*, and on the right end, *o′*, *o*, and *p*. The presence of molasses (containing raffinose) causes the faces *r′* to predominate over *c*, frequently to the complete exclusion of the latter. Likewise, considerable raffinose causes a long, slender prismatic development along the *b* axis, as shown on the extreme right of figure 118b. The presence of dextrose causes a thin plate-like development, the *a* faces greatly predominating over all others.

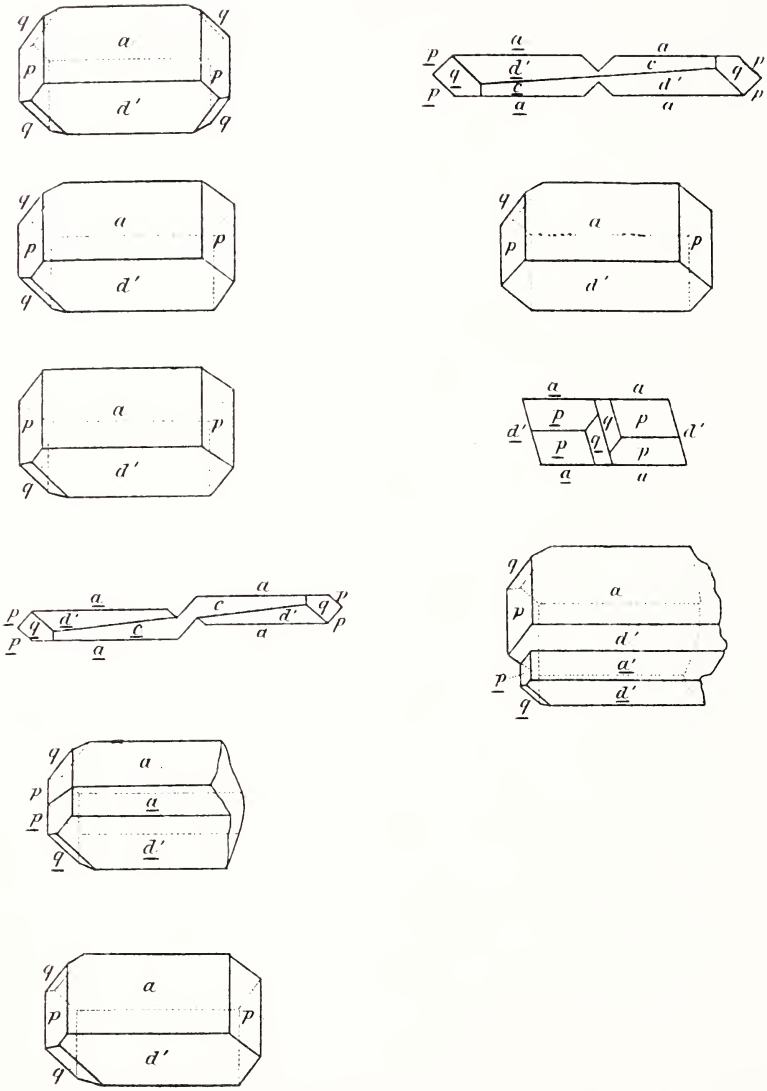

FIGURE 118.—*Drawings to illustrate growth and twinning habits of sucrose crystals.*

The letters used on the drawings identify the different crystal faces.

(a) Crystals grown from a pure sucrose solution.

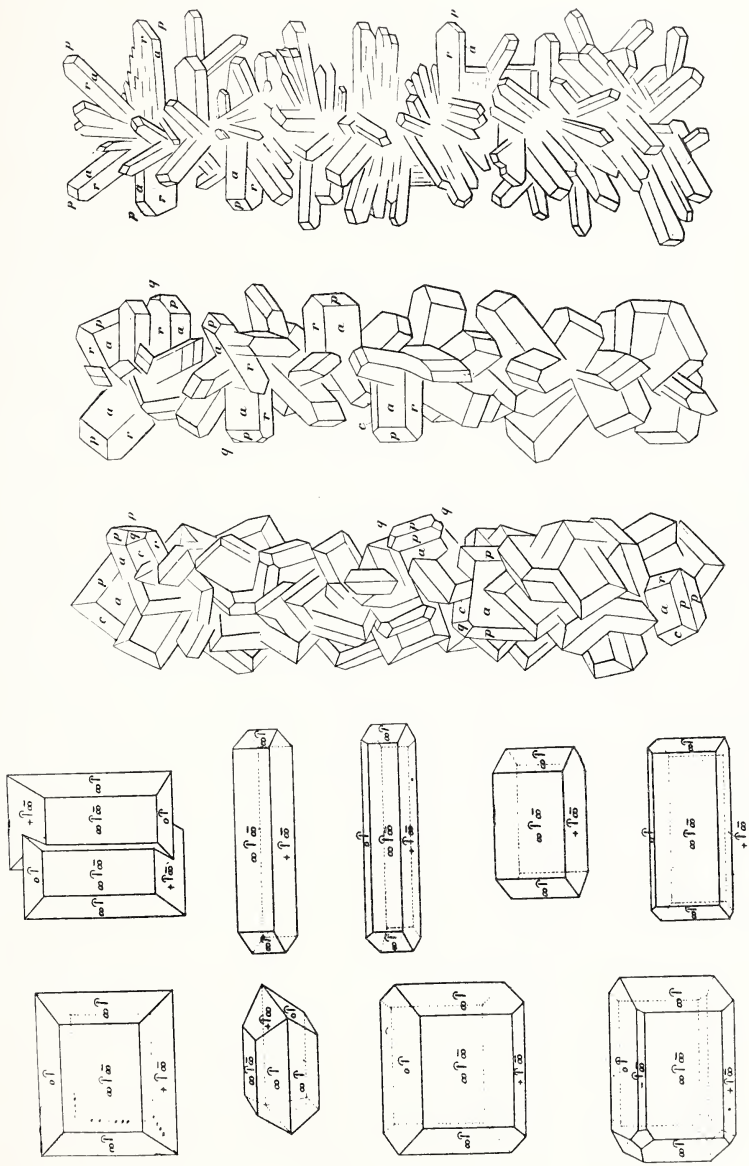

FIGURE 118.—(Continued).

(b) Crystals grown from a sucrose solution containing raffinose.

(b) α-DEXTROSE HYDRATE

Class: 4, Monoclinic sphenoidal.
Ratio of axes: $a:b:c=1.735:1:1.908$.
$\beta=97°59'$ (Becke) [15]
Solubility: One end disolves much more quickly than the other.
Plane of optic axes: b {010}
Median line: Approximately perpendicular to {101}.
Axial angle: Large.
Refractive indices: n_D, $\alpha=1.517$, $\beta=1.530$, $\gamma=1.555$.

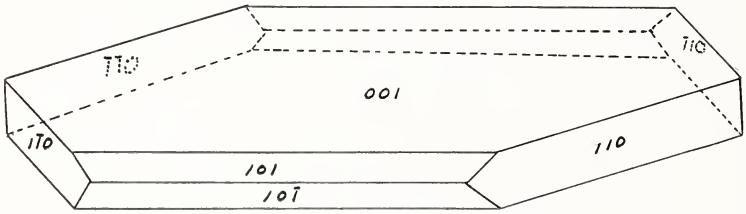

FIGURE 119.—*Dextrose hydrate crystal.*

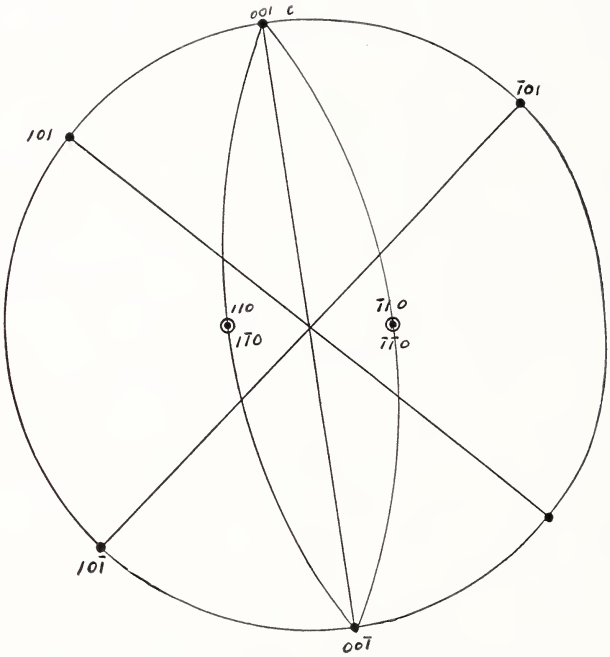

FIGURE 120.—*Stereographic net for dextrose hydrate.*

TABLE 67.—*Crystal forms of dextrose monohydrate*

Possible forms	Usual forms
Class 4 (see p. 534)	{001} {1$\bar{1}$0} {101} {10$\bar{1}$} {110}

TABLE 68.—*Angular values between faces of dextrose monohydrate crystals*

Face form letter	Millerian face symbol	Measured angle
m–m′	$(1\bar{1}0)-(110)$	60°24′
l–c	$(101)-(001)$	44°31′
d′–c	$(\bar{1}01)-(001)$	52°7′
m–c	$(1\bar{1}0)-(001)$	85°59′
m′–d′	$(\bar{1}\bar{1}0)-(101)$	69°27′
m–l	$(1\bar{1}0)-(101)$	66°27′

3. CHARACTERISTICS OF SYMMETRY CLASS 6 (RHOMBIC BISPHENOIDAL)

The rhombic or orthorhombic system is characterized by three rectangular axes, *a*, *b*, and *c*, all of unequal length.

$$a:b:c=?:1:? \qquad \alpha=\beta=\gamma=90°$$

Class 6 of this system is characterized by the fact that there are no planes of symmetry but that all three axes are axes of digonal symmetry. One-half of a complete revolution about any one of these three axes will restore the crystal to its original appearance. (See fig. 121.)

It is known as the bisphenoidal class, or digonal holoaxial type. The possible forms of this class are shown in table 69.

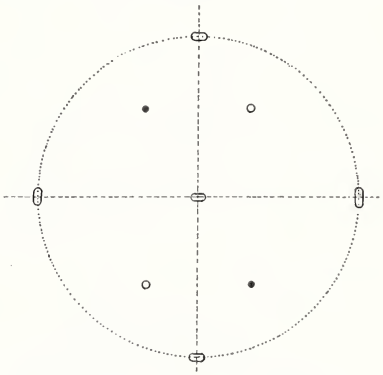

FIGURE 121.—*Symmetry elements of class 6.*

TABLE 69.—*Crystal forms of class 6*

Possible forms			
Form symbol	Millerian index	Number of faces	Name of geometrical figure which the form comprises
c	{001}	2	Basal pinacoid or third-order pinacoid.
a	{100}	2	Macropinacoid or first-order pinacoid.
b	{010}	2	Brachy pinacoid or second-order pinacoid.
p	{*hk*0}	4	Rhombic prism of the third order.
p or *m*	{110}	4	Do.
	{*h*0*l*}	4	Macro-domal prism of the second order.
r	{101}	4	Do.
q	{0*kl*}	4	Brachy domal prism.
	{011}	4	Rhombic prism of the first order.
o	{*hkl*}	4	Right rhombic sphenoid.
	{111}	4	Do.
o′	{$h\bar{k}l$}	4	Left rhombic sphenoid.
	{$1\bar{1}1$}	4	Do.

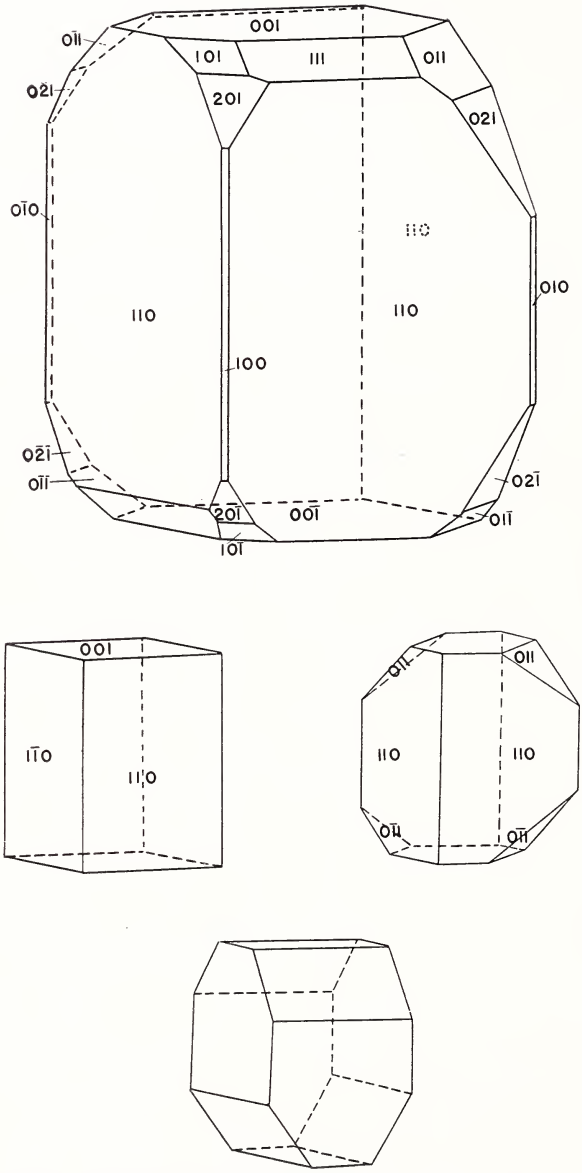

FIGURE 122.—*Levulose crystal showing different development of faces.*

In this class belong levulose, α-anhydrous dextrose, sorbose, mannose, trehalose, and raffinose.

(a) LEVULOSE

Crystal system: Orthorhombic.
Class 6: Rhombic bisphenoidal.
Symmetry type: Digonal holoaxial, characterized by three rectangular digonal axes of symmetry.
Habit: Prismatic.
Ratio of axes: $a:b:c=0.8007:1:0.9067$ (Schuster) [16].

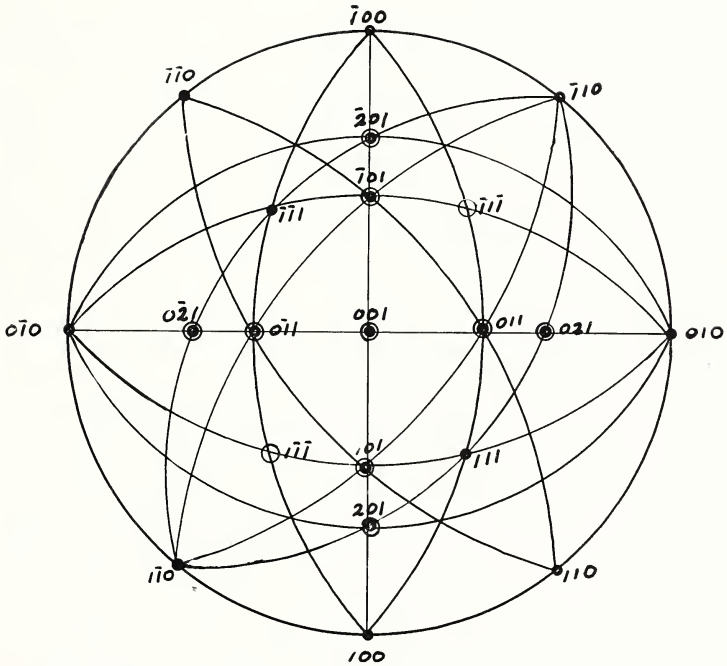

FIGURE 123.—*Stereographic net for levulose crystal.*

TABLE 70.—*Angular values between faces of levulose crystals*

Face form letter	Millerian face symbol	Measured angle
p–p	(110)–($1\bar{1}0$)	77°22′
q–q	(011)–($0\bar{1}1$)	84°24′
q–p	(011)–(110)	65°10′

Double refraction: Positive and very small.

$$\alpha=1.555+, \beta=1.555\pm, \gamma=1.555\mp.$$

Axial plane for red: c {001}
Axial plane for blue: b {010}
The axial angle is very small and becomes zero at certain wave lengths and temperatures so that the crystal appears uniaxial.

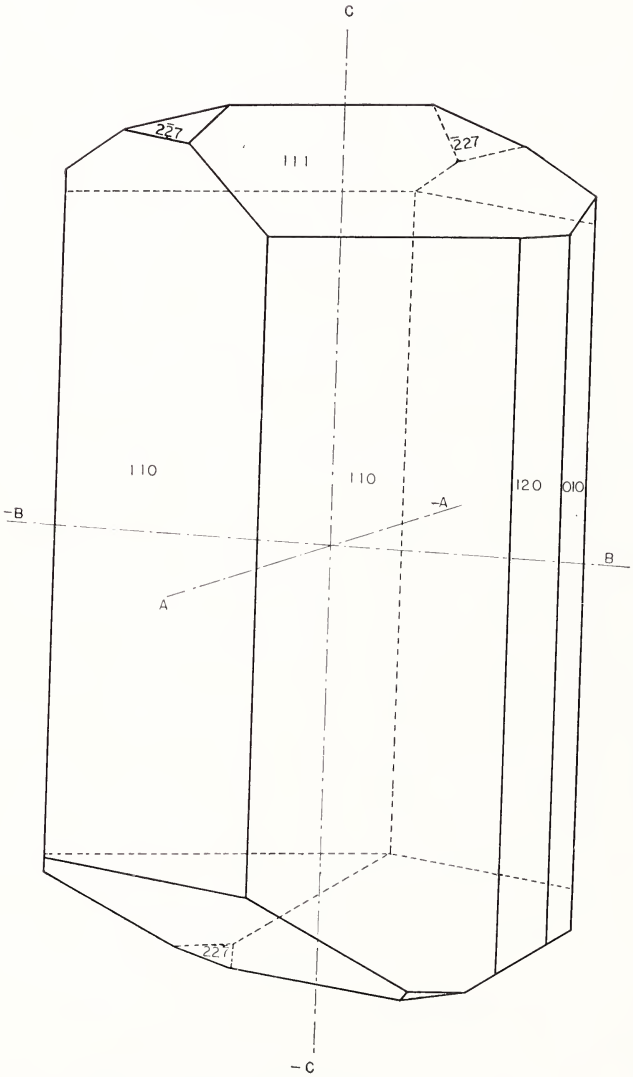

FIGURE 124.—*Anhydrous dextrose crystal.*

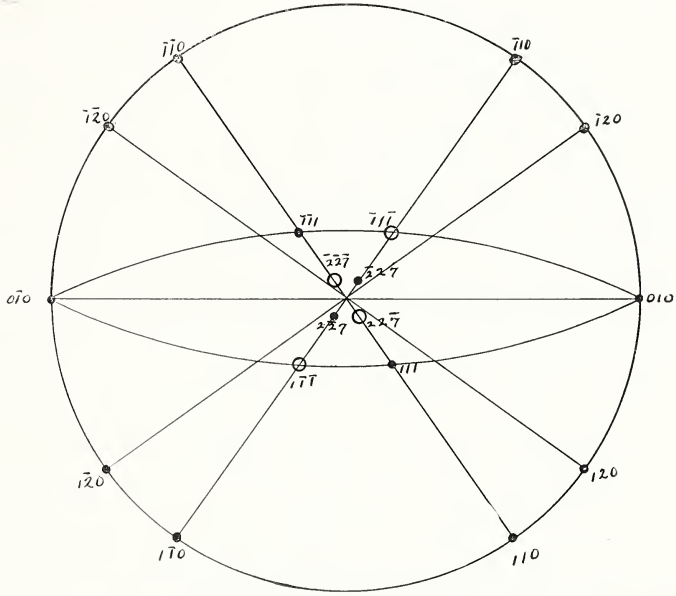

FIGURE 125.—*Stereographic net of anhydrous dextrose.*

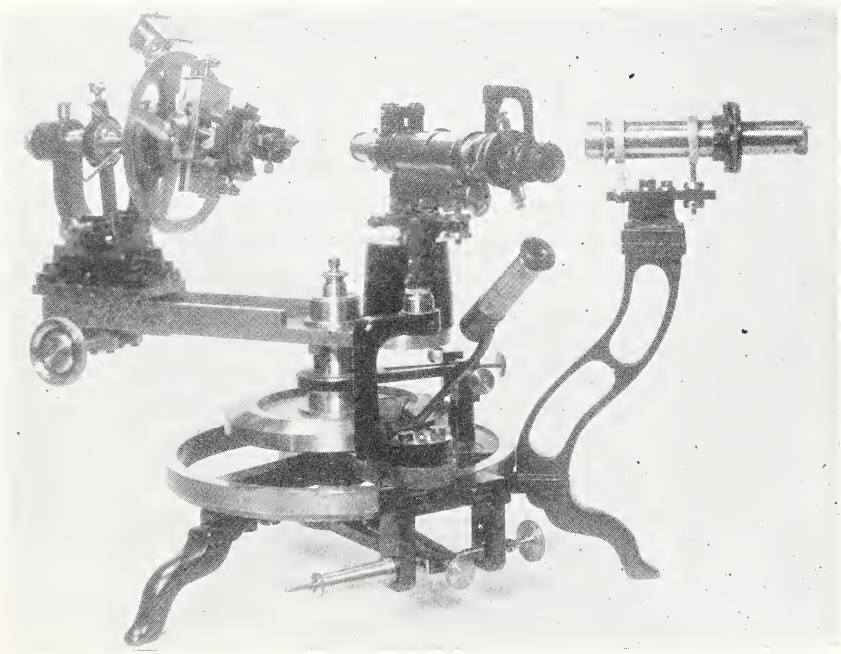

FIGURE 126.—*Goldschmidt two-circle goniometer used at the National Bureau of Standards.*

(b) α-DEXTROSE (ANHYDROUS)

Class 6: Rhombic bisphenoidal.
Ratio of axes: a: b: c=0.704:1:0.355 [15].
Plane of optic axis: a {100}.
Refractive indices: $\alpha=1.530$, $\beta=1.550$, $\gamma=1.560$.

TABLE 71.—*Crystal forms of anhydrous dextrose*

Possible forms	Usual forms
Same as levulose, see page 541, Table 69	*m*{110} *o*{111} *b*{010} *n*{120} $\zeta\{2\bar{2}7\}$

TABLE 72.—*Angular values between faces of anhydrous dextrose*

Face form letter	Millerian face symbol	Measured angle
m–*m'*	(110)–(110)	70°18′
o–*m*	(111)–(110)	59°47′
o–*m'*	(110)–(110)	80°1′
n–*m*	(120)–(110)	19°14′
ζ–*m'*	$(2\bar{2}7)$–(110)	80°17′

4. REFERENCES

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[2] W. H. Miller, Trans. Cambridge Phil. Soc. **7,** 209–216 (1842).
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[9] H. E. Merwin, Int. Crit. Tables **7,** 30 (1930).
[10] L. Longchambon, Bul. soc. Française minealogie **45,** 242 (1922).
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[14] L. Wulf, Z. Ver. deut. Zucker-Ind. **37,** 917 (1887); **38,** 226.
[15] F. Becke, Tschermak's mineralog. petrog. Mitt. **2,** 184 (1880); **10,** 464, 495 (1889). Absts. Z. Krist. **5,** 283; **20,** 298 (1888).
[16] M. J. Schuster, Tschermak's mineralog. petrog. Mitt. **9,** 216 (1888).

XXXIII. MELTING POINTS

1. GENERAL

The melting point is a valuable aid in the identification of purified sugars and their derivatives and also in the determination of the purity of these compounds. At any given pressure the solid and liquid phases of a substance are at equilibrium at a definite temperature. The presence of a small trace of impurity generally alters the melting point. Some substances, however, exist in more than one crystal

form and thereby have their melting points affected by the method of heating, thus making the melting point a less definite indication of purity. A number of different methods have been devised for making the melting point determination. Various types of melting point tubes are shown in figure 127.

2. CAPILLARY-TUBE METHODS

The simplest apparatus, illustrated by No. 1, consists of a round-bottomed tube of Pyrex or other suitable heat-resistant glass approximately 100 mm long, 30 mm inside diameter, and with walls not more than 1.5 mm thick at any point. The stirring device consists of a glass rod bent to form a ring at the bottom. The sample under test is in a capillary tube about 60 mm long, 0.8 to 1.2 mm inside diameter, with walls from 0.2 to 0.3 mm thick, and is closed at one end. In making the determination, place the finely powdered substance in the capillary tube by pushing the open end into the powder, and pack it

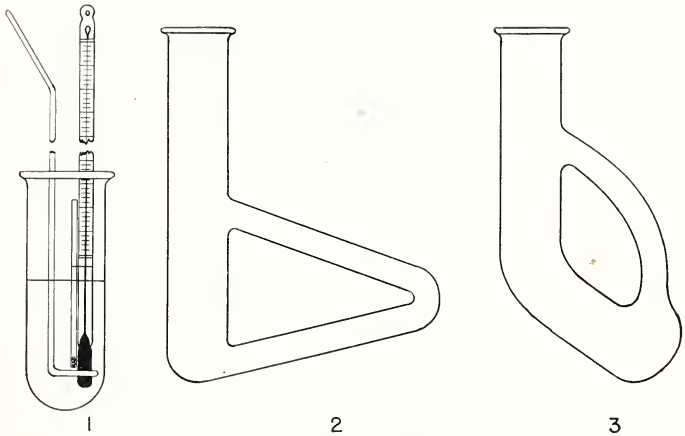

FIGURE 127.—*Types of melting-point tubes.*

down by moderate tapping on a solid surface. The sample should form a column about 3 mm in length when packed down. Attach the capillary to the thermometer by wetting them with the liquid of the bath or attach them by means of a piece of fine platinum wire. Adjust the position of the capillary so that the substance is centrally located by the side of the thermometer bulb. As a heating bath, fill the large tube with a suitable liquid such as sulfuric acid to a depth which will permit the top of the thermometer bulb to be immersed 20 to 30 mm below the surface of the liquid. Stir the bath constantly while heating slowly over a Bunsen flame or on an electric heater. Retard the rate of heating as the suspected melting point is approached, until finally the heating is so regulated that the rise in temperature is about 0.5 degree per minute. The temperature at which the substance liquifies is taken as the melting point.

In the method of the United States Pharmacopoeia [1] the temperature at which the column of substance in the capillary tube first begins to liquify at any point is defined as the beginning of melting, and the temperature at which the substance becomes liquid through-

out is defined as the end of melting. The usual precuations regarding the heating and stirring of the bath are observed. The result thus obtained as the melting interval is adjusted for the calibration correction of the thermometer and the correction for the emergent stem.

In this method the following liquids are suggested for use as heating baths: For temperatures up to 200° C, pure concentrated sulfuric acid; for temperatures up to about 350° C, a pure grade of cotton-seed oil (almost colorless). Other, though less desirable, substitutes for sulfuric acid at high temperatures are pure paraffin freshly distilled, and clean, white artificial (cotton-seed) lard. A very desirable bath for high temperature work is prepared by cautiously boiling together, for 5 or 10 minutes under a hood, a mixture of 70 parts of purified concentrated sulfuric acid and 30 parts of potassium sulfate, stirring constantly until the sulfate is completely dissolved.

In place of the simple tube described above, many workers prefer to use the Thiele melting-point tube (No. 2) or the Thiele-Dennis

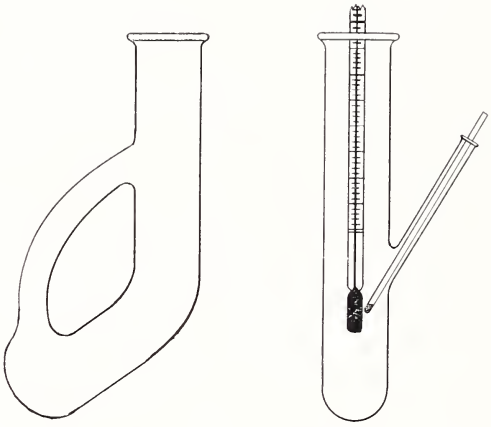

FIGURE 128.—*Melting-point tube.*

tube (No. 3). These tubes are so designed that heating causes a circulation of the liquid in the tube, making stirring unnecessary. A further modification (figure 128) consists of a tube similar to the above with a side tube sealed in at an angle of about 30° to the axis of the tube, which permits the capillary containing the sample to be inserted or removed without removing the thermometer. The use of the side arm also has the advantage that the capillary containing the sample can be placed in contact with the thermometer bulb and the usual unsatisfactory methods of fastening the capillary to the thermometer are eliminated. The various modifications of the Thiele tube and a discussion of their advantages are given in reference [2].

3. ADDITIONAL METHODS

Another method of determining melting points employs the Maquenne Block. This consists of a block of brass mounted in a frame above a long gas burner. In the top surface of the block are a number

of small cavities. A hole is bored lengthwise of the block, just below its upper surface, to permit the insertion of a thermometer.

To make a melting-point determination, place a small amount of the sample in one of the cavities and cover with a small glass plate. Insert the thermometer so that the bulb is just under the cavity containing the sample. Heat the block slowly until the substance begins to melt, then adjust the thermometer so that the mercury column just projects beyond the end of the block and note the temperature. As the block has approximately a uniform temperature, the stem correction of the emergent mercury column is eliminated.

Dennis and Shelton [3] have devised an apparatus for the accurate and rapid determination of melting points. It consists of an electric heater controlled by a rheostat and mounted on the end of a square pure copper bar. The temperature of this bar can be varied from room temperature to 300° C by means of the rheostat. A voltmeter shows the potential across the heater. The heat applied at one end of the bar causes a temperature gradation along the length of the bar, with a temperature variation of from 10° to 30° C. The temperature of the bar at any point is determined by turning a knob which lowers a constantan element onto the copper bar. This contact forms a thermocouple, the potential of which is read on a potentiometer graduated directly in degrees centigrade. To determine the melting point of a substance, drop a few finely ground particles along the surface of the bar. If the bar has been heated to the proper temperature, a distinct line of demarcation will be noted between the melted and unmelted particles. Move the knob along its slider and lower the constantan element onto the bar exactly at this line. Read the temperature directly by means of the potentiometer. The apparatus is claimed to give values for melting points to an accuracy of about 0.25° C.

4. REFERENCES

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[3] L. M. Dennis and R. S. Shelton, J. Am. Chem. Soc. **52** 3128 (1930).

PART 4. GENERAL INFORMATION

XXXIV. STANDARD SAMPLES

1. SUCROSE [44]

This Bureau is prepared to issue standard sucrose samples (see p. 392) prepared by recrystallization from aqueous solution or by precipitation with alcohol. For each sample, the process of purification has been continued until analysis shows a satisfactory product. A certificate of analysis accompanies the sample. The sugar usually contains but little moisture, and in a moderately dry atmosphere shows very little hygroscopicity. It is advisable to store the sample in a cool, dry place. If placed in a desiccator, the drying agent used should be pure. Vapors from impure sulfuric acid or phosphorus pentoxide frequently damage the sugar.

The uses of standard sucrose samples may be stated briefly as follows: (1) As a primary saccharimetric standard; (2) as a source of pure invert sugar for the standardization of analytical determinations of reducing sugar; (3) as a standard for the calibration of viscometers; and (4) as a material for standardization of bomb calorimeters. Sucrose has the advantage of being nonvolatile and nonhygroscopic. It is rather difficult to ignite and sometimes does not burn completely. It has a heat of combustion of about 3,950 calories, or only about half that of coal. The more exact value for each sample will be given in the certificate. For details of the standardization of bomb calorimeters, see NBS Circular C11.

2. DEXTROSE [45]

The standard dextrose samples are prepared by purification of the purest glucose of commerce in the manner described on page 390. A certificate of analysis will show the degree of purification of the sample. The standard dextrose sample is intended to assist in research work of a general nature and, in particular, to serve as a standard reducing sugar for analytical work.

XXXV. TESTS

1. SPECIAL

The special requirements of scientific investigators, manufacturers of apparatus, and others, for higher precision than is considered in the following schedules, will be met as far as the regular work of the Bureau will permit. The application for a special test should state fully the purpose for which the apparatus has been used or is to be used in the future, the need for the test, and the precision desired. The test should be arranged for by correspondence before shipment of the apparatus. The special fee charged will depend chiefly upon the time consumed and the amount of alteration required in the regular Bureau testing set-ups. An estimate will be given when possible.

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[44], [45] See list on p. 559.

2. GENERAL INSTRUCTIONS TO APPLICANTS FOR TESTS

(a) APPLICATION FOR TEST

The request for test should be made in writing, addressed to the National Bureau of Standards, Washington, D. C., and should enumerate the articles submitted for test, giving the identification marks of each—for example, maker's name and number—and should state the nature of the test desired.

(b) NATURE OF TEST

The classification of tests in this Circular should be followed, and the schedule numbers should be used to indicate the test desired. When the desired test is not included under the regular schedules, the applicant must comply with the requirements for special tests. When apparatus is sent simply for test, without definite instructions, the Bureau will, if practicable, decide upon the nature of the test.

(c) IDENTIFICATION MARKS

All packages should bear the shipper's name and address and, when convenient, a list of the contents.

Each separate piece of apparatus or sample of material should be provided with an identification mark, which in many cases may be the maker's name and number. The identification mark should be given in the application for the test.

(d) SHIPPING DIRECTIONS

Apparatus or test specimens should be securely packed in cases or packages which will not be broken in transportation. The shipment in both directions is at the applicant's risk. To facilitate packing and shipping, the tops of the cases should have the return or forwarding address on the underside and should be put on with screws. Transportation charges are payable by the party desiring the test and must be prepaid. Unless otherwise arranged, articles will be returned or forwarded by express collect.

(e) RETURN OF APPARATUS

Regular tests will be made in the order in which the applications are received, except as this practice may be varied by grouping similar tests together. It is suggested, therefore, that the applicant, if possible, make request for a test from 2 weeks to 2 months preceding the shipment of the apparatus. This facilitates the work of the Bureau as well as the prompt return of the apparatus.

(f) ADDRESS

Apparatus submitted for test, as well as all correspondence, should be addressed to the National Bureau of Standards, Washington, D. C. Apparatus delivered in person or by messenger should be accompanied by a written request for the test.

(g) REMITTANCES

Fees should be sent with the request for test, in accordance with the following schedules, or promptly upon receipt of bill. Certificates are not given nor is apparatus returned until the fees due thereon have been received. Remittances may be made by money order or check drawn to the order of the National Bureau of Standards.

3. CERTIFICATES AND STATEMENTS

Apparatus that fulfills the requirements for certification will be tested and given a certificate of corrections. The certificate can only indicate the corrections of the apparatus at the time of the test and does not guarantee the constancy of the values. When there are defects which exclude an apparatus from certification, a report will be issued instead of a certificate, in which such information as has been found will be stated.

4. TEST-FEE SCHEDULES [46]

Effective July 1, 1940, superseding all previous schedules for the items covered.

TEST FEE SCHEDULE 421.—*Polariscopes for absolute measurement—Circular scales*

Item	Description	Fee
421a	Polariscopes for absolute measurement: Determination of true value of five to ten points ±0.01°, with critical examination of optical parts	$7. 50
421b	Polariscopes for absolute measurement: Determination of true value of five to ten points ±0.002°, with critical examination of optical parts	12. 50
421c	Eliptic analyzers. Price according to precision required, minimum charge	2. 00

TEST FEE SCHEDULE 422.—*Elliptic analyzers and physical properties of glass*

Item	Description	Fee
422a	Glass: Determining the softening points and annealing ranges up to 800° C	$25. 00
422b	Determining deformability up to 700° C and over a range of not more than 50° C	60. 00

TEST FEE SCHEDULE 423.—*Quartz control plates and polariscope cover glasses*

Items	Description	Fee
	Quartz control plates:	
423a	Certification of rotation in circular degrees, "yellow-green mercury line" (λ=546.1 mμ) and sodium lines (λ=589.25 mμ) at 20° C	$3. 00
423b	Certification of same in circular degrees and sugar degrees at 20° C	4. 00
423c	Certification of rotation at other temperatures by special arrangement.	
423d	Test of quartz control plates rejected, each (see 423y)	. 25
423e	Table of sucrose corrections for temperature	2. 00
	Cover glasses:	
423f	Absence of double refraction, each (see 423y)	. 10
423y	Minimum total charge billed for any test	2. 00

[46] For special tests not covered by these schedules, fees will be charged dependent on the nature of the test. Copies of certificates or reports previously issued or reissue of worn or damaged certificates or reports returned, each 25 cents; minimum fee, $1.00.

TEST FEE SCHEDULE 424.—*Saccharimeters*

Item	Description	Fee
	Single quartz wedge:	
424a	Certification at five points	$6. 50
424b	Adjustment and certification at five points	12. 50 to 35. 00
	Double quartz wedge:	
424c	Certification at five points on positive wedge and three points on negative wedge	9. 00
424d	Certification at five points on each wedge	10. 00
424e	Adjustment and certification at five points for each wedge	15. 00 to 35. 00
	Laurent type:	
424f	Certification at five points	7. 50
	Other types:	
424g	Certification at price according to condition.	

TEST FEE SCHEDULE 425.—*Sugars and other materials*

Item	Description	Fee
	Raw sugars and molasses:	
425a	Direct polarization	$3. 00
425b	Clerget polarization by acid inversion	5. 00
	Raw sugars:	
425c	Clerget polarization by invertase	6. 00
425d	Polarization at 87° C	6. 00
	Reducing sugars:	
425e	Determination of	4. 00
	Sugar:	
425f	Moisture determination	2. 00
425g	Ash determination	3. 00
	Molasses:	
425h	Determination of specific gravity or weight per gallon	4. 00
425i	Determination of moisture	4. 00
425z	Determination of purity of purified sucrose, dextrose, and other sugars; optical rotation for any substance; or for special tests not covered by the above schedule, fees will be charged dependent upon the nature of the test.	

TEST FEE SCHEDULE 311 (EXTRACT).—*Laboratory thermometers*

Item	Description	Fee
311a	Thermometers, testing at points in the interval 0° to 100° C (32° to 212° F) for each point tested	$0. 50
311b	Thermometers, testing at points above 100° and up to 300° C, or above 212° and up to 600° F, for each point tested	. 75
311c	Thermometers, testing at points above 300° C or above 600° F, for each point tested	2. 00
311d	Thermometers, testing at points in the interval 0° to −35° C or 32° to −35° F, for each point tested	2. 50
	Items (a) to (d), inclusive, apply particularly to the types of thermometers listed in tables 1, 2, 3, and 4 of Bureau Circular C8, 3d or 4th ed.	
311e	Calorimetric thermometers, testing at intervals of 2° C or 5° F	5. 00
311f	Beckmann thermometers, with 5° or 6° C scale, testing at 1° intervals by comparison with precision standards	6. 00

TEST FEE SCHEDULE 311 (EXTRACT).—*Laboratory thermometers*—Continued

Item	Description	Fee
311ff	Beckmann thermometers, calibration by means of mercury threads and comparison with precision standards, with the highest accuracy warranted by the construction and action of the thermometer	$12. 00
	Unless the request for test of a Beckmann thermometer specifies test under 311ff, the instrument will be tested under item 311f. Thermometers so constructed that unusual difficulty is encountered in separating mercury threads for calibration will be eligible for test only under item 311f. There is somewhat greater danger of breakage in tests under 311ff than in tests under 311f. Beckmann thermometers with scales longer than 6° will be subject to special fees.	
311j	Thermocouples for temperatures between −40° and 500° C minimum charge each	10. 00
311k	Thermocouples for range −40° to 500° C, calibration per point	3. 00
	Items (j) and (k) do not cover tests of multiple junction assemblies.	
	Items (g) to (k), inclusive, refer to tests described in National Bureau of Standards Circular C8, 3d or 4th ed.	
311m	When instruments submitted are found by preliminary tests to be unsuitable for test, a charge will be made to cover the cost of the preliminary work. Minimum fee	1. 00
311y	Minimum fee on any test or transaction	1. 00

TEST FEE SCHEDULE 297.—*Polariscope Tubes*

Item	Description	Fee
297c	Polariscope tubes—	
	Determination of the average length of a polariscope observation tube and marking with NBS serial number if length is within ±0.04 mm of the nominal value:	
	(1) 100-mm tubes, each	$1. 00
	(2) 200-mm tubes, each	1. 00
	(3) 400-mm tubes, each	2. 00
297d	Same, when four or more of the same size are submitted at the same time:	
	(1) 100-mm tubes, each	. 75
	(2) 200-mm tubes, each	. 75
	(3) 400-mm tubes, each	1. 50
297e	Polariscope tubes—	
	Determination of average length of 100 and 200 mm polariscope observation tubes to ±0.01 mm	
	(1) 100-mm tubes, each	1. 50
	(2) 200-mm tubes, each	2. 00
297f	Same, when four or more of the same size are submitted at the same time:	
	(1) 100-mm tubes, each	1. 15
	(2) 200 mm tubes, each	1. 50
297g	Polariscope tubes—	
	Determination of average length of 400 mm polariscope observation tube to ±0.02 mm, each	3. 00
297h	Same, when four or more are submitted at the same time, each	2. 25
297y	Minimum total charge billed for any test	2. 00

TEST FEE SCHEDULE 225.—*"Class M" laboratory standards of mass*

[NOTE.—Item b applies to weights which are boiled in distilled water to remove traces of plating salts as completely as possible, and also as a test of the adequacy of the plating. Item a applies to weights which are not given this treatment, particularly to those that are not electroplated or that have been in use for some years.]

Item	Description	Fee
225a	Class M standards that are not new or not plated: For each set, or single weight, or group that is submitted, tested and certified or reported as a unit—	
	For regular inspection, cleaning, handling, etc. (but not including test for accuracy)	$1.00
225b	New plated class M standards and sets or groups containing such standards: For each set, or single weight, or group of weights that is submitted, tested, and certified or reported as a unit—	
	For regular inspection, cleaning, handling, etc. (but not including test for accuracy)	2.00
	(Note.—To the appropriate item above there will be added, in the case of a full regular test, an amount computed from one or more of the following items—the item or items used depending on the nature of the test. For weights given the complete inspection, cleaning, etc. but not tested for accuracy, on account of defects discovered or for some other cause, the fee is only the appropriate one of the items above.)	
225d	Moderate precision test of each weight—	
	Testing accuracy and certifying or reporting of correction for each weight	.75
225j	High precision test of each weight—	
	Testing accuracy and certifying or reporting of correction for each weight (as a rule this test requires also the determination of the volume of each weight above 1 g. See item v)	1.00
225v	For each weight for which the actual volume must be determined—	
	Determination of actual volume by hydrostatic weighings	1.50
225w	Reference standards and weights whose constancy over a long period of time must be assured—	
	Determination of change that occurs during 3 months under good atmospheric conditions. The fee for this test of constancy with "age" will be equal to (and in addition to) that computed from item d or j.	
225y	Minimum total charge billed for any test	2.00

TEST FEE SCHEDULE 226.—*"Class S" laboratory weights*

Item	Description	Fee
226a	Class S laboratory weights that are "one-piece" weights, or screw knob weights that are not plated or lacquered, or in general, weights that do not need to be given a test for the effect of changes in atmospheric humidity: For each set or single weight, or group that is submitted, tested and certified or reported as a unit—	
	For regular inspection, cleaning, handling, etc. (but not including test for accuracy)	$1.00
226b	Plated or lacquered screw knob weights or sets or groups that include such weights; or in general, weights that are tested for the effect of variations in atmospheric humidity:	
	For each set, or single weight, or group that is submitted tested and certified or reported as a unit—	
	For regular inspection, cleaning, handling, etc. (but not including test for accuracy)	3.00
	[NOTE.—To the appropriate item above there will be added, in the case of a full regular test, an amount computed from either item d or item g depending on the nature of the test.	
	For weights given the complete inspection, cleaning, etc., but not tested for accuracy, on account of defects discovered or for some other cause, the fee is only the appropriate one of the items above.]	
226d	Determination of actual value for each weight—	
	Testing and certifying or reporting of actual correction for each weight	.75
226g	Tolerance test of each weight—	
	Testing and certifying or reporting whether each weight is correct within the specified tolerance	.40
226y	Minimum total charge billed for any test	2.00

TEST FEE SCHEDULE 227.—*"Class S2" laboratory weights*

This schedule covers a new class, including what are often called "second quality analytical weights," "students' sets," and other laboratory weights of similar quality and of accuracy within five times the tolerances for weights of class S.

Item	Description	Fee
227a	Class S2 laboratory weights, for each set or single weight, or group that is submitted, tested, and certified or reported as a unit—	
	For regular inspection, cleaning, handling, etc. (but not including tests for accuracy)	$1.00
	[NOTE.—To the item above there will be added, in the case of a full regular test, an amount computed from item g.	
	For weights given the complete inspection, cleaning, etc., but not tested for accuracy, on account of defects discovered or for some other cause, the fee is only item a.]	
227g	Tolerance test of each weight—	
	Testing and certifying or reporting whether each weight is correct within the specified tolerance	.30
227y	Minimum total charge billed for any test	2.00

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TEST FEE SCHEDULE 241 (extract).—*Volumetric apparatus*

Item	Description	Fee
241a	Flasks of capacities up to and including 250 ml—	
	Testing and stamping, each flask	$0. 40
241b	Flasks of capacities above 250 ml—	
	Testing and stamping, each capacity tested	. 75
241c	Transfer pipettes and Babcock test bottles—	
	Testing and stamping, each capacity tested	. 50
241d	Cylindrical graduates—	
	Testing and stamping, each interval tested	. 40
241e	Specific gravity flasks—	
	Testing and stamping, each capacity tested	. 40
241f	Certificates of capacity for any of above, when requested, additional, each	. 60
	(In general, certificates are not issued for the above.)	
241g	Burettes—	
	Testing and certifying five intervals	2. 50
241h	Measuring pipettes—	
	Testing and certifying five intervals	2. 25
241i	Burettes and measuring pipettes—	
	Testing and certifying capacity of additional intervals, each additional interval	. 40
241l	Apparatus intended for temperatures other than 20° C, between 15° and 30° C—	
	Testing, additional charge for each piece	. 25
241m	Apparatus of indicated capacity other than in milliliters—	
	Testing, additional charge for each piece	. 25
241n	Apparatus disqualified for test—	
	Preliminary examination, charge for each piece	. 20
241o	Missing identification numbers—	
	For supplying, charge for each number	. 25
241y	Minimum total charge billed for any test	2. 00

TEST FEE SCHEDULE 243 (extract).—*Hydrometers and thermohydrometers*

Item	Description	Fee
243a	Hydrometer—	
	Test to determine whether or not it complies with Bureau requirements for precision stamp	$1. 50
243b	Thermohydrometer, as under (a)—	
	Test including test of thermometer scale	2. 25
243c	Corrections—	
	Certification at three points on either or both scales, additional fee	. 60
243d	Additional points certified, each	. 50
243e	Instrument—	
	Determination of weight, additional fee	. 50
243f	Missing identification numbers—	
	supplying, charges per number	. 25

Standard sugar samples

Standard Sample No.	Description	Fee
17	Sucrose ..... 60 grams	$2.00
41	Dextrose ..... 70 grams	2.00

PART 5.—APPENDIXES

XXXVI. APPENDIX 1.—TABLES 73 TO 150

[Additional literature references to accompany some of the tables are given on page 693.]

TABLE 73.—*Formulas for calculating specific rotations (concentration variable)*

c = concentration in grams per 100 ml.
p = percentage by weight.
q = percentage of water.

Sugar	Formula
Sucrose	$[\alpha]_D^{20} = 66.462 + 0.0087c - 0.000235c^2$ [1].
Dextrose	$[\alpha]_D^{20} = 52.50 + 0.0188p + 0.000517p^2$.
Dextrose	$[\alpha]_{5461A}^{20} = 62.032 + 0.04257c$ [2].
Dextrose	$[\alpha]_{5461A}^{20} = 62.032 + 0.04220p + 0.0001897p^2$ [2].
Fructose	$[\alpha]_D^{20} = -113.96 + 0.258q$.
Maltose	$[\alpha]_D^{20} = 138.475 - 0.01837p$.
Lactose	$[\alpha]_D^{20} = 52.53$.
Invert sugar	$[\alpha]_D^{20} = -(19.415 + 0.07065c - 0.00054c^2)$ [3].
Invert sugar temperature correction	$[\alpha]_D^{t} = [\alpha]_D^{20} + (0.283 + 0.0014c)(t - 20°C)$ [3].

REFERENCES

[1] This Circular, p. 82.
[2] R. F. Jackson, Bul. BS **13,** 633 (1916) S293.
[3] F. W. Zerban, J. Am. Chem. Soc. **47,** 1104 (1925).

TABLE 74.—*Rotatory power of dextrose and corrections to be applied to saccharimeter readings* [1]

Scale reading	Correction to be added	Rotation per gram of dextrose	Scale reading	Correction to be added	Rotation per gram of dextrose
° S	° S	° S	° S	° S	° S
100	0	3.1026	50	0.55	3.0688
95	.10	3.0993	45	.54	3.0658
90	.20	3.0957	40	.53	3.0621
85	.28	3.0924	35	.50	3.0589
80	.35	3.0890	30	.46	3.0559
75	.41	3.0858	25	.41	3.0525
70	.46	3.0823	20	.35	3.0492
65	.50	3.0790	15	.28	3.0457
60	.52$_5$	3.0757	10	.20	3.0414
55	.54	3.0725	5	.10	3.0414
------	--------	--------	2	.05	3.0257

[1] Based on the normal weight 32.231 g (air, brass weights) at 20° C. R. F. Jackson, Bul. BS **13,** 36 (1916) S293.

TABLE 75.—*Specific rotation* ($[\alpha]_D^{20}$) *of certain sugars at various concentrations*

Concentration	Sucrose	Dextrose	Fructose	Maltose	Lactose hydrate
%	%	%	%	%	
5	66.500	52.607	−89.42	138.38	52.53.
10	66.527	52.740	−90.72	138.29	Remains unchanged at all concentrations.
15	66.541	52.898	−92.01	138.20	
20	66.540	53.083	−93.30	138.11	
25	66.523	53.293	−94.59	138.02	
30	66.487	53.529	−95.88	137.92	
35	66.432	53.791	−97.18	137.82	
40	66.351	54.079	−98.47	--------	
45	66.245	54.393	--------	--------	
50	66.109	54.732	--------	--------	

TABLE 76.—*Rotatory power of invert sugar*[1]

Weight in 100 ml	$[\alpha]_D^{20}$	Rotation of invert sugar per gram at 20° C	Weight in 100 ml	$[\alpha]_D^{20}$	Rotation of invert sugar per gram at 20° C
g	*degrees*	°*S*	*g*	*degrees*	°*S*
1	−19.693	−1.1377	14	−20.162	−1.1648
2	[1]19.729	[1]1.1397	16	[1]20.235	[1]1.1690
4	[1]19.801	[1]1.1439	18	[1]20.307	[1]1.1731
6	[1]19.874	[1]1.1481	20	[1]20.379	[1]1.1773
8	[1]19.946	[1]1.1523	22	[1]20.451	[1]1.1815
10	[1]20.018	[1]1.1564	24	[1]20.523	[1]1.1856
12	[1]20.090	[1]1.1606	26	[1]20.596	[1]1.1898

[1] Calculated from Gubb's equation. Ber. deut. Chem. Ges. **18**, 2207 (1885).

TABLE 77.—*Coefficients*[1] *in the Creydt raffinose formula*

$$S=\frac{aP-bP'}{bc},\ R=\frac{P-S}{1.852}.$$

[If both polarizations have the same temperature, use column *bc*. If polarized at different temperatures, multiply *b* at t_1 (of direct polarization) by *c* at t_2 (of invert polarization). To the whole denominator, add 0.000794 ($m-13$), in which *m* is the dry substance taken for inversion and contained in a final volume of 100 ml].

Temperature (°*C*)			Basic Clerget divisor						Raffinose denominator
			133.00		133.18		133.29		
	a	*b*	*c*	*bc*	*c*	*bc*	*c*	*bc*	
16	0.5068	1.0012	0.8568	0.8578	0.8586	0.8596	0.8597	0.8607	1.854
17	.5086	1.0009	.8536	.8544	.8554	.8562	.8565	.8573	1.854
18	.5104	1.0006	.8504	.8509	.8522	.8527	.8533	.8538	1.853
19	.5122	1.0003	.8472	.8475	.8490	.8493	.8501	.8504	1.853
20	.5140	1.0000	.8440	.8440	.8458	.8458	.8469	.8469	1.852
21	.5158	0.9997	.8408	.8406	.8426	.8423	.8437	.8434	1.851
22	.5176	.9994	.8376	.8371	.8394	.8389	.8405	.8400	1.851
23	.5194	.9991	.8344	.8337	.8362	.8354	.8373	.8365	1.850
24	.5212	.9988	.8312	.8302	.8330	.8320	.8341	.8331	1.850
25	.5230	.9985	.8280	.8268	.8298	.8286	.8309	.8297	1.849
26	.5248	.9982	.8248	.8233	.8266	.8251	.8277	.8262	1.849
27	.5266	.9979	.8216	.8199	.8234	.8217	.8245	.8228	1.848
28	.5284	.9976	.8184	.8164	.8202	.8182	.8213	.8193	1.848
29	.5302	.9973	.8152	.8130	.8170	.8148	.8181	.8159	1.847
30	.5320	.9970	.8120	.8096	.8138	.8114	.8149	.8125	1.846

[1] See p. 143 of text.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*

[The original values of Munson and Walker [1] have been redetermined and the values in this table for dextrose, invert sugar, and the sucrose and invert-sugar mixtures totaling 0.4 and 2.0 g are the values redetermined by Hammond.[2] The values for levulose and the 0.3-g total-sugar mixture of sucrose and invert sugar are new values determined by Hammond.[2] The values for lactose and the two lactose and sucrose mixtures are those of Straughn and Given,[3] which have been calculated to even intervals of copper. The values for maltose are those determined by Walker [4]]

Values of National Bureau of Standards (Hammond) [5]

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
10	11. 3	4. 6	5. 2	3. 2	2. 9	--------	5. 1
11	12. 4	5. 1	5. 7	3. 7	3. 4	--------	5. 6
12	13. 5	5. 6	6. 2	4. 2	3. 9	--------	6. 1
13	14. 6	6. 0	6. 7	4. 8	4. 4	--------	6. 7
14	15. 8	6. 5	7. 2	5. 3	4. 9	--------	7. 2
15	16. 9	7. 0	7. 7	5. 8	5. 4	--------	7. 7
16	18. 0	7. 5	8. 2	6. 3	5. 9	--------	8. 3
17	19. 1	8. 0	8. 7	6. 8	6. 4	--------	8. 8
18	20. 3	8. 5	9. 2	7. 3	6. 9	--------	9. 3
19	21. 4	8. 9	9. 7	7. 8	7. 4	--------	9. 9
20	22. 5	9. 4	10. 2	8. 3	7. 9	1. 9	10. 4
21	23. 6	9. 9	10. 7	8. 8	8. 4	2. 4	10. 9
22	24. 8	10. 4	11. 2	9. 3	8. 9	2. 9	11. 5
23	25. 9	10. 9	11. 7	9. 9	9. 5	3. 4	12. 0
24	27. 0	11. 4	12. 3	10. 4	10. 0	3. 9	12. 5
25	28. 1	11. 9	12. 8	10. 9	10. 5	4. 4	13. 1
26	29. 3	12. 3	13. 3	11. 4	11. 0	4. 9	13. 6
27	30. 4	12. 8	13. 8	11. 9	11. 5	5. 5	14. 2
28	31. 5	13. 3	14. 3	12. 4	12. 0	6. 0	14. 7
29	32. 6	13. 8	14. 8	12. 9	12. 5	6. 5	15. 2
30	33. 8	14. 3	15. 3	13. 4	13. 0	7. 0	15. 8
31	34. 9	14. 8	15. 8	14. 0	13. 5	7. 5	16. 3
32	36. 0	15. 3	16. 3	14. 5	14. 1	8. 0	16. 8
33	37. 2	15. 7	16. 8	15. 0	14. 6	8. 5	17. 4
34	38. 3	16. 2	17. 3	15. 5	15. 1	9. 0	17. 9
35	39. 4	16. 7	17. 8	16. 0	15. 6	9. 5	18. 4
36	40. 5	17. 2	18. 3	16. 5	16. 1	10. 1	19. 0
37	41. 7	17. 7	18. 9	17. 0	16. 6	10. 6	19. 5
38	42. 8	18. 2	19. 4	17. 6	17. 1	11. 1	20. 1
39	43. 9	18. 7	19. 9	18. 1	17. 6	11. 6	20. 6
40	45. 0	19. 2	20. 4	18. 6	18. 2	12. 1	21. 1
41	46. 2	19. 7	20. 9	19. 1	18. 7	12. 6	21. 7
42	47. 3	20. 1	21. 4	19. 6	19. 2	13. 1	22. 2
43	48. 4	20. 6	21. 9	20. 1	19. 7	13. 7	22. 8
44	49. 5	21. 1	22. 4	20. 7	20. 2	14. 2	23. 3
45	50. 7	21. 6	22. 9	21. 2	20. 7	14. 7	23. 8
46	51. 8	22. 1	23. 5	21. 7	21. 3	15. 2	24. 4
47	52. 9	22. 6	24. 0	22. 2	21. 8	15. 7	24. 9
48	54. 0	23. 1	24. 5	22. 7	22. 3	16. 2	25. 4
49	55. 2	23. 6	25. 0	23. 2	22. 8	16. 8	26. 0

See footnotes at end of table.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

[The original values of Munson and Walker [1] have been redetermined and the values in this table for dextrose, invert sugar, and the sucrose and invert-sugar mixtures totaling 0.4 and 2.0 g are the values redetermined by Hammond.[2] The values for levulose and the 0.3-g total-sugar mixture of sucrose and invert sugar are new values determined by Hammond.[2] The values for lactose and the two lactose and sucrose mixtures are those of Straughn and Given,[3] which have been calculated to even intervals of copper. The values for maltose are those determined by Walker [4]]

Values of Straughn and Given					Values of Walker
Copper	Cuprous oxide	Lactose.H_2O	Lactose.H_2O and sucrose: 1 lactose 4 sucrose	Lactose.H_2O and sucrose: 1 lactose 12 sucrose	Maltose.H_2O
mg	*mg*	*mg*	*mg*	*mg*	*mg*
10	11. 3	7. 1	6. 9	----------	7. 2
11	12. 4	7. 8	7. 5	----------	8. 2
12	13. 5	8. 5	8. 2	----------	9. 1
13	14. 6	9. 2	8. 9	----------	10. 1
14	15. 8	9. 9	9. 6	----------	11. 0
15	16. 9	10. 6	10. 2	----------	11. 9
16	18. 0	11. 3	10. 9	----------	12. 9
17	19. 1	12. 0	11. 6	----------	13. 8
18	20. 3	12. 7	12. 3	----------	14. 8
19	21. 4	13. 4	12. 9	----------	15. 7
20	22. 5	14. 1	13. 6	----------	16. 7
21	23. 6	14. 8	14. 3	----------	17. 6
22	24. 8	15. 5	15. 0	----------	18. 5
23	25. 9	16. 2	15. 7	----------	19. 5
24	27. 0	16. 9	16. 4	----------	20. 4
25	28. 1	17. 6	17. 1	----------	21. 4
26	29. 3	18. 4	17. 8	----------	22. 3
27	30. 4	19. 1	18. 4	----------	23. 2
28	31. 5	19. 8	19. 1	----------	24. 2
29	32. 6	20. 5	19. 8	----------	25. 1
30	33. 8	21. 2	20. 5	----------	26. 0
31	34. 9	22. 0	21. 3	----------	27. 0
32	36. 0	22. 8	22. 0	----------	27. 9
33	37. 2	23. 6	22. 8	----------	28. 9
34	38. 3	24. 3	23. 5	----------	29. 8
35	39. 4	25. 1	24. 3	----------	30. 8
36	40. 5	25. 9	25. 0	----------	31. 7
37	41. 7	26. 6	25. 7	----------	32. 7
38	42. 8	27. 4	26. 5	----------	33. 6
39	43. 9	28. 2	27. 2	----------	34. 5
40	45. 0	28. 9	28. 0	----------	35. 5
41	46. 2	29. 7	28. 7	----------	36. 4
42	47. 3	30. 5	29. 5	----------	37. 3
43	48. 4	31. 3	30. 2	----------	38. 3
44	49. 5	32. 0	31. 0	----------	39. 2
45	50. 7	32. 8	31. 7	----------	40. 1
46	51. 8	33. 5	32. 5	----------	41. 0
47	52. 9	34. 3	33. 2	----------	42. 0
48	54. 0	35. 1	34. 0	----------	42. 9
49	55. 2	35. 9	34. 7	----------	43. 8

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of National Bureau of Standards (Hammond)

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
50	56. 3	24. 1	25. 5	23. 8	23. 3	17. 3	26. 5
51	57. 4	24. 6	26. 0	24. 3	23. 8	17. 8	27. 1
52	58. 5	25. 1	26. 5	24. 8	24. 3	18. 3	27. 6
53	59. 7	25. 6	27. 0	25. 3	24. 9	18. 8	28. 2
54	60. 8	26. 1	27. 6	25. 8	25. 4	19. 3	28. 7
55	61. 9	26. 5	28. 1	26. 3	25. 9	19. 9	29. 2
56	63. 0	27. 0	28. 6	26. 9	26. 4	20. 4	29. 8
57	64. 2	27. 5	29. 1	27. 4	26. 9	20. 9	30. 3
58	65. 3	28. 0	29. 6	27. 9	27. 5	21. 4	30. 9
59	66. 4	28. 5	30. 1	28. 4	28. 0	21. 9	31. 4
60	67. 6	29. 0	30. 6	28. 9	28. 5	22. 5	31. 9
61	68. 7	29. 5	31. 2	29. 5	29. 0	23. 0	32. 5
62	69. 8	30. 0	31. 7	30. 0	29. 5	23. 5	33. 0
63	70. 9	30. 5	32. 2	30. 5	30. 1	24. 0	33. 6
64	72. 1	31. 0	32. 7	31. 0	30. 6	24. 5	34. 1
65	73. 2	31. 5	33. 2	31. 6	31. 1	25. 1	34. 7
66	74. 3	32. 0	33. 7	32. 1	31. 6	25. 6	35. 2
67	75. 4	32. 5	34. 3	32. 6	32. 1	26. 1	35. 8
68	76. 6	33. 0	34. 8	33. 1	32. 7	26. 6	36. 3
69	77. 7	33. 5	35. 3	33. 6	33. 2	27. 1	36. 8
70	78. 8	34. 0	35. 8	34. 2	33. 7	27. 7	37. 4
71	79. 9	34. 5	36. 3	34. 7	34. 2	28. 2	37. 9
72	81. 1	35. 0	36. 8	35. 2	34. 7	28. 7	38. 5
73	82. 2	35. 5	37. 4	35. 7	35. 3	29. 2	39. 0
74	83. 3	36. 0	37. 9	36. 3	35. 8	29. 8	39. 6
75	84. 4	36. 5	38. 4	36. 8	36. 3	30. 3	40. 1
76	85. 6	37. 0	38. 9	37. 3	36. 8	30. 8	40. 7
77	86. 7	37. 5	39. 4	37. 8	37. 4	31. 3	41. 2
78	87. 8	38. 0	40. 0	38. 4	37. 9	31. 9	41. 7
79	88. 9	38. 5	40. 5	38. 9	38. 4	32. 4	42. 3
80	90. 1	39. 0	41. 0	39. 4	38. 9	32. 9	42. 8
81	91. 2	39. 5	41. 5	39. 9	39. 5	33. 4	43. 4
82	92. 3	40. 0	42. 0	40. 5	40. 0	34. 0	43. 9
83	93. 4	40. 5	42. 6	41. 0	40. 5	34. 5	44. 5
84	94. 6	41. 0	43. 1	41. 5	41. 0	35. 0	45. 0
85	95. 7	41. 5	43. 6	42. 0	41. 6	35. 5	45. 6
86	96. 8	42. 0	44. 1	42. 6	42. 1	36. 1	46. 1
87	97. 9	42. 5	44. 7	43. 1	42. 6	36. 6	46. 7
88	99. 1	43. 0	45. 2	43. 6	43. 1	37. 1	47. 2
89	100. 2	43. 5	45. 7	44. 1	43. 7	37. 6	47. 8
90	101. 3	44. 0	46. 2	44. 7	44. 2	38. 2	48. 3
91	102. 5	44. 5	46. 7	45. 2	44. 7	38. 7	48. 9
92	103. 6	45. 0	47. 3	45. 7	45. 2	39. 2	49. 4
93	104. 7	45. 5	47. 8	46. 3	45. 8	39. 8	50. 0
94	105. 8	46. 0	48. 3	46. 8	46. 3	40. 3	50. 5

See footnotes at end of table.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of Straughn and Given					Values of Walker
Copper	Cuprous oxide	Lactose.H_2O	Lactose.H_2O and sucrose: 1 lactose 4 sucrose	Lactose.H_2O and sucrose: 1 lactose 12 sucrose	Maltose.H_2O
mg	*mg*	*mg*	*mg*	*mg*	*mg*
50	56. 3	36. 6	35. 5	----------	44. 8
51	57. 4	37. 4	36. 2	----------	45. 7
52	58. 5	38. 2	37. 0	----------	46. 7
53	59. 7	39. 0	37. 7	----------	47. 6
54	60. 8	39. 7	38. 5	----------	48. 6
55	61. 9	40. 4	39. 2	----------	49. 5
56	63. 0	41. 2	40. 0	----------	50. 4
57	64. 2	42. 0	40. 7	----------	51. 4
58	65. 3	42. 8	41. 5	39. 0	52. 3
59	66. 4	43. 6	42. 2	39. 7	53. 2
60	67. 6	44. 4	43. 0	40. 5	54. 2
61	68. 7	45. 1	43. 7	41. 1	55. 2
62	69. 8	45. 9	44. 5	41. 8	56. 1
63	70. 9	46. 7	45. 2	42. 4	57. 1
64	72. 1	47. 4	46. 0	43. 1	58. 0
65	73. 2	48. 2	46. 7	43. 8	58. 9
66	74. 3	49. 0	47. 5	44. 4	59. 9
67	75. 4	49. 7	48. 2	45. 1	60. 8
68	76. 6	50. 5	49. 0	45. 7	61. 8
69	77. 7	51. 3	49. 7	46. 4	62. 7
70	78. 8	52. 1	50. 5	47. 1	63. 7
71	79. 9	52. 8	51. 2	47. 7	64. 6
72	81. 1	53. 6	52. 0	48. 4	65. 5
73	82. 2	54. 3	52. 7	49. 1	66. 5
74	83. 3	55. 1	53. 5	49. 7	67. 4
75	84. 4	55. 9	54. 2	50. 4	68. 4
76	85. 6	56. 7	55. 0	51. 0	69. 3
77	86. 7	57. 5	55. 7	51. 7	70. 2
78	87. 8	58. 2	56. 5	52. 4	71. 2
79	88. 9	59. 0	57. 2	53. 1	72. 1
80	90. 1	59. 8	58. 0	53. 8	73. 1
81	91. 2	60. 5	58. 7	54. 4	74. 0
82	92. 3	61. 3	59. 5	55. 1	74. 9
83	93. 4	62. 1	60. 2	55. 7	75. 9
84	94. 6	62. 9	61. 0	56. 4	76. 8
85	95. 7	63. 6	61. 7	57. 0	77. 8
86	96. 8	64. 4	62. 5	57. 7	78. 7
87	97. 9	65. 2	63. 2	58. 4	79. 6
88	99. 1	66. 0	64. 0	59. 1	80. 6
89	100. 2	66. 7	64. 7	59. 7	81. 5
90	101. 3	67. 5	65. 5	60. 4	82. 5
91	102. 5	68. 3	66. 3	61. 1	83. 4
92	103. 6	69. 1	67. 0	61. 8	84. 3
93	104. 7	69. 8	67. 8	62. 4	85. 3
94	105. 8	70. 6	68. 5	63. 1	86. 2

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of National Bureau of Standards (Hammond)

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
95	107. 0	46. 5	48. 8	47. 3	46. 8	40. 8	51. 1
96	108. 1	47. 0	49. 4	47. 8	47. 4	41. 3	51. 6
97	109. 2	47. 5	49. 9	48. 4	47. 9	41. 9	52. 2
98	110. 3	48. 0	50. 4	48. 9	48. 4	42. 4	52. 7
99	111. 5	48. 5	50. 9	49. 4	48. 9	42. 9	53. 3
100	112. 6	49. 0	51. 5	50. 0	49. 5	43. 5	53. 8
101	113. 7	49. 5	52. 0	50. 5	50. 0	44. 0	54. 4
102	114. 8	50. 0	52. 5	51. 0	50. 5	44. 5	54. 9
103	116. 0	50. 6	53. 0	51. 6	51. 1	45. 1	55. 5
104	117. 1	51. 1	53. 6	52. 1	51. 6	45. 6	56. 0
105	118. 2	51. 6	54. 1	52. 6	52. 1	46. 1	56. 6
106	119. 3	52. 1	54. 6	53. 1	52. 7	46. 7	57. 1
107	120. 5	52. 6	55. 2	53. 7	53. 2	47. 2	57. 7
108	121. 6	53. 1	55. 7	54. 2	53. 7	47. 7	58. 2
109	122. 7	53. 6	56. 2	54. 7	54. 2	48. 3	58. 8
110	123. 8	54. 1	56. 7	55. 3	54. 8	48. 8	59. 3
111	125. 0	54. 6	57. 3	55. 8	55. 3	49. 3	59. 9
112	126. 1	55. 1	57. 8	56. 3	55. 8	49. 9	60. 4
113	127. 2	55. 6	58. 3	56. 9	56. 4	50. 4	61. 0
114	128. 3	56. 1	58. 9	57. 4	56. 9	50. 9	61. 6
115	129. 5	56. 7	59. 4	57. 9	57. 4	51. 5	62. 1
116	130. 6	57. 2	59. 9	58. 5	58. 0	52. 0	62. 7
117	131. 7	57. 7	60. 4	59. 0	58. 5	52. 5	63. 2
118	132. 8	58. 2	61. 0	59. 5	59. 0	53. 1	63. 8
119	134. 0	58. 7	61. 5	60. 1	59. 6	53. 6	64. 3
120	135. 1	59. 2	62. 0	60. 6	60. 1	54. 1	64. 9
121	136. 2	59. 7	62. 6	61. 2	60. 7	54. 7	65. 4
122	137. 4	60. 2	63. 1	61. 7	61. 2	55. 2	66. 0
123	138. 5	60. 7	63. 6	62. 2	61. 7	55. 8	66. 5
124	139. 6	61. 3	64. 2	62. 8	62. 3	56. 3	67. 1
125	140. 7	61. 8	64. 7	63. 3	62. 8	56. 8	67. 7
126	141. 9	62. 3	65. 2	63. 8	63. 3	57. 4	68. 2
127	143. 0	62. 8	65. 8	64. 4	63. 9	57. 9	68. 8
128	144. 1	63. 3	66. 3	64. 9	64. 4	58. 4	69. 3
129	145. 2	63. 8	66. 8	65. 4	64. 9	59. 0	69. 9
130	146. 4	64. 3	67. 4	66. 0	65. 5	59. 5	70. 4
131	147. 5	64. 9	67. 9	66. 5	66. 0	60. 1	71. 0
132	148. 6	65. 4	68. 4	67. 1	66. 6	60. 6	71. 6
133	149. 7	65. 9	69. 0	67. 6	67. 1	61. 1	72. 1
134	150. 9	66. 4	69. 5	68. 1	67. 6	61. 7	72. 7
135	152. 0	66. 9	70. 0	68. 7	68. 2	62. 2	73. 2
136	153. 1	67. 4	70. 6	69. 2	68. 7	62. 8	73. 8
137	154. 2	68. 0	71. 1	69. 8	69. 3	63. 3	74. 3
138	155. 4	68. 5	71. 6	70. 3	69. 8	63. 9	74. 9
139	156. 5	69. 0	72. 2	70. 8	70. 3	64. 4	75. 5

See footnotes at end of table.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of Straughn and Given					Values of Walker
			Lactose.H_2O and sucrose		
Copper	Cuprous oxide	Lactose.H_2O	1 lactose 4 sucrose	1 lactose 12 sucrose	Maltose.H_2O
mg	*mg*	*mg*	*mg*	*mg*	*mg*
95	107. 0	71. 4	69. 3	63. 8	87. 2
96	108. 1	72. 2	70. 0	64. 4	88. 1
97	109. 2	72. 9	70. 8	65. 1	89. 0
98	110. 3	73. 7	71. 5	65. 8	90. 0
99	111. 5	74. 5	72. 3	66. 4	90. 9
100	112. 6	75. 2	73. 0	67. 1	91. 8
101	113. 7	76. 0	73. 8	67. 7	92. 8
102	114. 8	76. 8	74. 5	68. 4	93. 7
103	116. 0	77. 6	75. 3	69. 1	94. 7
104	117. 1	78. 4	76. 1	69. 7	95. 6
105	118. 2	79. 1	76. 8	70. 4	96. 6
106	119. 3	79. 8	77. 5	71. 1	97. 5
107	120. 5	80. 6	78. 3	71. 8	98. 4
108	121. 6	81. 4	79. 1	72. 5	99. 4
109	122. 7	82. 2	79. 8	73. 1	100. 3
110	123. 8	83. 0	80. 6	73. 8	101. 3
111	125. 0	83. 8	81. 3	74. 5	102. 2
112	126. 1	84. 5	82. 1	75. 2	103. 1
113	127. 2	85. 3	82. 8	75. 8	104. 1
114	128. 3	86. 1	83. 6	76. 5	105. 0
115	129. 5	86. 8	84. 3	77. 2	106. 0
116	130. 6	87. 6	85. 1	77. 9	106. 9
117	131. 7	88. 4	85. 9	78. 5	107. 8
118	132. 8	89. 2	86. 6	79. 2	108. 8
119	134. 0	90. 0	87. 4	79. 9	109. 7
120	135. 1	90. 7	88. 1	80. 6	110. 6
121	136. 2	91. 5	88. 9	81. 2	111. 6
122	137. 4	92. 3	89. 6	81. 9	112. 5
123	138. 5	93. 0	90. 4	82. 6	113. 5
124	139. 6	93. 8	91. 2	83. 3	114. 4
125	140. 7	94. 6	91. 9	84. 0	115. 3
126	141. 9	95. 4	92. 7	84. 6	116. 3
127	143. 0	96. 1	93. 4	85. 3	117. 2
128	144. 1	96. 9	94. 2	86. 0	118. 1
129	145. 2	97. 7	94. 9	86. 7	119. 1
130	146. 4	98. 5	95. 7	87. 3	120. 0
131	147. 5	99. 2	96. 4	88. 0	120. 9
132	148. 6	100. 0	97. 2	88. 7	121. 9
133	149. 7	100. 8	98. 0	89. 4	122. 8
134	150. 9	101. 5	98. 8	90. 1	123. 8
135	152. 0	102. 3	99. 5	90. 8	124. 7
136	153. 1	103. 1	100. 2	91. 5	125. 6
137	154. 2	103. 9	101. 0	92. 1	126. 6
138	155. 4	104. 7	101. 7	92. 8	127. 5
139	156. 5	105. 4	102. 5	93. 5	128. 4

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of National Bureau of Standards (Hammond)

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
140	157. 6	69. 5	72. 7	71. 4	70. 9	64. 9	76. 0
141	158. 7	70. 0	73. 2	71. 9	71. 4	65. 5	76. 6
142	159. 9	70. 5	73. 8	72. 5	72. 0	66. 0	77. 1
143	161. 0	71. 1	74. 3	73. 0	72. 5	66. 6	77. 7
144	162. 1	71. 6	74. 9	73. 5	73. 0	67. 1	78. 3
145	163. 2	72. 1	75. 4	74. 1	73. 6	67. 7	78. 8
146	164. 4	72. 6	75. 9	74. 6	74. 1	68. 2	79. 4
147	165. 5	73. 1	76. 5	75. 2	74. 7	68. 7	80. 0
148	166. 6	73. 7	77. 0	75. 7	75. 2	69. 3	80. 5
149	167. 8	74. 2	77. 6	76. 3	75. 7	69. 8	81. 1
150	168. 9	74. 7	78. 1	76. 8	76. 3	70. 4	81. 6
151	170. 0	75. 2	78. 6	77. 3	76. 8	70. 9	82. 2
152	171. 1	75. 7	79. 2	77. 9	77. 4	71. 5	82. 8
153	172. 3	76. 3	79. 7	78. 4	77. 9	72. 0	83. 3
154	173. 4	76. 8	80. 3	79. 0	78. 5	72. 6	83. 9
155	174. 5	77. 3	80. 8	79. 5	79. 0	73. 1	84. 4
156	175. 6	77. 8	81. 3	80. 1	79. 6	73. 7	85. 0
157	176. 8	78. 3	81. 9	80. 6	80. 1	74. 2	85. 6
158	177. 9	78. 9	82. 4	81. 2	80. 6	74. 8	86. 1
159	179. 0	79. 4	83. 0	81. 7	81. 2	75. 3	86. 7
160	180. 1	79. 9	83. 5	82. 2	81. 7	75. 9	87. 3
161	181. 3	80. 4	84. 0	82. 8	82. 3	76. 4	87. 8
162	182. 4	81. 0	84. 6	83. 3	82. 8	77. 0	88. 4
163	183. 5	81. 5	85. 1	83. 9	83. 4	77. 5	89. 0
164	184. 6	82. 0	85. 7	84. 4	83. 9	78. 1	89. 5
165	185. 8	82. 5	86. 2	85. 0	84. 5	78. 6	90. 1
166	186. 9	83. 1	86. 8	85. 5	85. 0	79. 2	90. 6
167	188. 0	83. 6	87. 3	86. 1	85. 6	79. 7	91. 2
168	189. 1	84. 1	87. 8	86. 6	86. 1	80. 3	91. 8
169	190. 3	84. 6	88. 4	87. 2	86. 7	80. 8	92. 3
170	191. 4	85. 2	88. 9	87. 7	87. 2	81. 4	92. 9
171	192. 5	85. 7	89. 5	88. 3	87. 8	81. 9	93. 5
172	193. 6	86. 2	90. 0	88. 8	88. 3	82. 5	94. 0
173	194. 8	86. 7	90. 6	89. 4	88. 9	83. 0	94. 6
174	195. 9	87. 3	91. 1	89. 9	89. 4	83. 6	95. 2
175	197. 0	87. 8	91. 7	90. 5	90. 0	84. 1	95. 7
176	198. 1	88. 3	92. 2	91. 0	90. 5	84. 7	96. 3
177	199. 3	88. 9	92. 8	91. 6	91. 1	85. 2	96. 9
178	200. 4	89. 4	93. 3	92. 1	91. 6	85. 8	97. 4
179	201. 5	89. 9	93. 8	92. 7	92. 2	86. 3	98. 0
180	202. 7	90. 4	94. 4	93. 2	92. 7	86. 9	98. 6
181	203. 8	91. 0	94. 9	93. 8	93. 3	87. 4	99. 2
182	204. 9	91. 5	95. 5	94. 3	93. 8	88. 0	99. 7
183	206. 0	92. 0	96. 0	94. 9	94. 4	88. 6	100. 3
184	207. 2	92. 6	96. 6	95. 4	94. 9	89. 1	100. 9

See footnotes at end of table.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of Straughn and Given					Values of Walker
			Lactose.H_2O and sucrose		
Copper	Cuprous oxide	Lactose.H_2O	1 lactose 4 sucrose	1 lactose 12 sucrose	Maltose.H_2O
mg	*mg*	*mg*	*mg*	*mg*	*mg*
140	157. 6	106. 2	103. 2	94. 2	129. 4
141	158. 7	107. 0	104. 0	94. 8	130. 3
142	159. 9	107. 8	104. 8	95. 5	131. 3
143	161. 0	108. 5	105. 5	96. 2	132. 2
144	162. 1	109. 3	106. 3	96. 9	133. 1
145	163. 2	110. 1	107. 0	97. 6	134. 1
146	164. 4	110. 9	107. 8	98. 2	135. 0
147	165. 5	111. 7	108. 5	98. 9	135. 9
148	166. 6	112. 4	109. 3	99. 6	136. 9
149	167. 8	113. 2	110. 0	100. 3	137. 8
150	168. 9	114. 0	110. 8	100. 9	138. 8
151	170. 0	114. 8	111. 6	101. 6	139. 7
152	171. 1	115. 5	112. 3	102. 3	140. 6
153	172. 3	116. 3	113. 1	103. 0	141. 6
154	173. 4	117. 1	113. 8	103. 7	142. 5
155	174. 5	117. 9	114. 6	104. 4	143. 4
156	175. 6	118. 6	115. 3	105. 1	144. 4
157	176. 8	119. 4	116. 1	105. 8	145. 3
158	177. 9	120. 2	116. 9	106. 4	146. 3
159	179. 0	121. 0	117. 6	107. 1	147. 2
160	180. 1	121. 7	118. 4	107. 8	148. 1
161	181. 3	122. 5	119. 2	108. 5	149. 1
162	182. 4	123. 3	119. 9	109. 1	150. 0
163	183. 5	124. 0	120. 7	109. 8	150. 9
164	184. 6	124. 8	121. 5	110. 5	151. 9
165	185. 8	125. 6	122. 2	111. 1	152. 8
166	186. 9	126. 4	123. 0	111. 8	153. 8
167	188. 0	127. 2	123. 7	112. 5	154. 7
168	189. 1	128. 0	124. 5	113. 2	155. 6
169	190. 3	128. 7	125. 3	113. 9	156. 6
170	191. 4	129. 5	126. 0	114. 6	157. 5
171	192. 5	130. 3	126. 8	115. 3	158. 4
172	193. 6	131. 0	127. 5	116. 0	159. 4
173	194. 8	131. 8	128. 3	116. 7	160. 3
174	195. 9	132. 6	129. 1	117. 3	161. 3
175	197. 0	133. 4	129. 8	118. 0	162. 2
176	198. 1	134. 2	130. 6	118. 7	163. 1
177	199. 3	134. 9	131. 4	119. 4	164. 1
178	200. 4	135. 7	132. 1	120. 1	165. 0
179	201. 5	136. 5	132. 9	120. 7	166. 0
180	202. 7	137. 3	133. 7	121. 4	166. 9
181	203. 8	138. 0	134. 4	122. 1	167. 8
182	204. 9	138. 8	135. 2	122. 8	168. 8
183	206. 0	139. 6	135. 9	123. 5	169. 7
184	207. 2	140. 4	136. 7	124. 2	170. 6

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of National Bureau of Standards (Hammond)

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
185	208. 3	93. 1	97. 1	96. 0	95. 5	89. 7	101. 4
186	209. 4	93. 6	97. 7	96. 5	96. 0	90. 2	102. 0
187	210. 5	94. 2	98. 2	97. 1	96. 6	90. 8	102. 6
188	211. 7	94. 7	98. 8	97. 6	97. 1	91. 3	103. 1
189	212. 8	95. 2	99. 3	98. 2	97. 7	91. 9	103. 7
190	213. 9	95. 7	99. 9	98. 7	98. 2	92. 4	104. 3
191	215. 0	96. 3	100. 4	99. 3	98. 8	93. 0	104. 8
192	216. 2	96. 8	101. 0	99. 9	99. 4	93. 6	105. 4
193	217. 3	97. 3	101. 5	100. 4	99. 9	94. 1	106. 0
194	218. 4	97. 9	102. 1	101. 0	100. 5	94. 7	106. 6
195	219. 5	98. 4	102. 6	101. 5	101. 0	95. 2	107. 1
196	220. 7	98. 9	103. 2	102. 1	101. 6	95. 8	107. 7
197	221. 8	99. 5	103. 7	102. 6	102. 1	96. 4	108. 3
198	222. 9	100. 0	104. 3	103. 2	102. 7	96. 9	108. 8
199	224. 0	100. 5	104. 8	103. 7	103. 2	97. 5	109. 4
200	225. 2	101. 1	105. 4	104. 3	103. 8	98. 0	110. 0
201	226. 3	101. 6	106. 0	104. 9	104. 4	98. 6	110. 6
202	227. 4	102. 2	106. 5	105. 4	104. 9	99. 2	111. 1
203	228. 5	102. 7	107. 1	106. 0	105. 5	99. 7	111. 7
204	229. 7	103. 2	107. 6	106. 5	106. 0	100. 3	112. 3
205	230. 8	103. 8	108. 2	107. 1	106. 6	100. 9	112. 9
206	231. 9	104. 3	108. 7	107. 6	107. 2	101. 4	113. 4
207	233. 1	104. 8	109. 3	108. 2	107. 7	102. 0	114. 0
208	234. 2	105. 4	109. 8	108. 8	108. 3	102. 5	114. 6
209	235. 3	105. 9	110. 4	109. 3	108. 8	103. 1	115. 2
210	236. 4	106. 5	110. 9	109. 9	109. 4	103. 7	115. 7
211	237. 6	107. 0	111. 5	110. 4	110. 0	104. 2	116. 3
212	238. 7	107. 5	112. 1	111. 0	110. 5	104. 8	116. 9
213	239. 8	108. 1	112. 6	111. 6	111. 1	105. 4	117. 5
214	240. 9	108. 6	113. 2	112. 1	111. 6	105. 9	118. 0
215	242. 1	109. 2	113. 7	112. 7	112. 2	106. 5	118. 6
216	243. 2	109. 7	114. 3	113. 2	112. 8	107. 1	119. 2
217	244. 3	110. 2	114. 9	113. 8	113. 3	107. 6	119. 8
218	245. 4	110. 8	115. 4	114. 4	113. 9	108. 2	120. 3
219	246. 6	111. 3	116. 0	114. 9	114. 4	108. 8	120. 9
220	247. 7	111. 9	116. 5	115. 5	115. 0	109. 3	121. 5
221	248. 8	112. 4	117. 1	116. 1	115. 6	109. 9	122. 1
222	249. 9	112. 9	117. 6	116. 6	116. 1	110. 5	122. 6
223	251. 1	113. 5	118. 2	117. 2	116. 7	111. 0	123. 2
224	252. 2	114. 0	118. 8	117. 7	117. 3	111. 6	123. 8
225	253. 3	114. 6	119. 3	118. 3	117. 8	112. 2	124. 4
226	254. 4	115. 1	119. 9	118. 9	118. 4	112. 7	125. 0
227	255. 6	115. 7	120. 4	119. 4	119. 0	113. 3	125. 5
228	256. 7	116. 2	121. 0	120. 0	119. 5	113. 9	126. 1
229	257. 8	116. 7	121. 6	120. 6	120. 1	114. 4	126. 7

See footnotes at end of table.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of Straughn and Given					Values of Walker
			Lactose.H_2O and sucrose		
Copper	Cuprous oxide	Lactose.H_2O	1 lactose 4 sucrose	1 lactose 12 sucrose	Maltose.H_2O
mg	*mg*	*mg*	*mg*	*mg*	*mg*
185	208. 3	141. 2	137. 5	124. 9	171. 6
186	209. 4	141. 9	138. 2	125. 6	172. 5
187	210. 5	142. 7	139. 0	126. 3	173. 4
188	211. 7	143. 5	139. 8	127. 0	174. 4
189	212. 8	144. 3	140. 6	127. 7	175. 3
190	213. 9	145. 0	141. 3	128. 3	176. 3
191	215. 0	145. 8	142. 1	129. 0	177. 2
192	216. 2	146. 6	142. 8	129. 7	178. 1
193	217. 3	147. 4	143. 6	130. 4	179. 1
194	218. 4	148. 2	144. 3	131. 1	180. 0
195	219. 5	149. 0	145. 1	131. 8	180. 9
196	220. 7	149. 8	145. 9	132. 5	181. 9
197	221. 8	150. 5	146. 6	133. 2	182. 8
198	222. 9	151. 3	147. 4	133. 9	183. 8
199	224. 0	152. 0	148. 1	134. 6	184. 7
200	225. 2	152. 8	148. 9	135. 3	185. 6
201	226. 3	153. 6	149. 7	136. 0	186. 6
202	227. 4	154. 4	150. 5	136. 6	187. 5
203	228. 5	155. 2	151. 2	137. 3	188. 5
204	229. 7	156. 0	152. 0	138. 0	189. 4
205	230. 8	156. 8	152. 8	138. 7	190. 4
206	231. 9	157. 5	153. 5	139. 4	191. 3
207	233. 1	158. 3	154. 3	140. 1	192. 2
208	234. 2	159. 1	155. 0	140. 8	193. 1
209	235. 3	159. 8	155. 8	141. 5	194. 1
210	236. 4	160. 6	156. 5	142. 2	195. 0
211	237. 6	161. 4	157. 3	142. 9	195. 9
212	238. 7	162. 2	158. 1	143. 6	196. 9
213	239. 8	163. 0	158. 8	144. 3	197. 8
214	240. 9	163. 8	159. 6	145. 0	198. 8
215	242. 1	164. 5	160. 4	145. 7	199. 7
216	243. 2	165. 3	161. 1	146. 4	200. 6
217	244. 3	166. 1	161. 9	147. 1	201. 6
218	245. 4	166. 9	162. 7	147. 8	202. 5
219	246. 6	167. 7	163. 4	148. 4	203. 5
220	247. 7	168. 5	164. 2	149. 1	204. 4
221	248. 8	169. 3	165. 0	149. 8	205. 3
222	249. 9	170. 0	165. 7	150. 5	206. 3
223	251. 1	170. 8	166. 5	151. 2	207. 2
224	252. 2	171. 6	167. 3	151. 9	208. 1
225	253. 3	172. 3	168. 0	152. 6	209. 1
226	254. 4	173. 1	168. 8	153. 3	210. 0
227	255. 6	173. 9	169. 6	154. 0	211. 0
228	256. 7	174. 7	170. 4	154. 7	211. 9
229	257. 8	175. 5	171. 2	155. 4	212. 8

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TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of National Bureau of Standards (Hammond)

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
230	258. 9	117. 3	122. 1	121. 1	120. 7	115. 0	127. 3
231	260. 1	117. 8	122. 7	121. 7	121. 2	115. 6	127. 9
232	261. 2	118. 4	123. 3	122. 3	121. 8	116. 2	128. 4
233	262. 3	118. 9	123. 8	122. 8	122. 4	116. 7	129. 0
234	263. 4	119. 5	124. 4	123. 4	122. 9	117. 3	129. 6
235	264. 6	120. 0	124. 9	124. 0	123. 5	117. 9	130. 2
236	265. 7	120. 6	125. 5	124. 5	124. 1	118. 4	130. 8
237	266. 8	121. 1	126. 1	125. 1	124. 6	119. 0	131. 3
238	268. 0	121. 7	126. 6	125. 7	125. 2	119. 6	131. 9
239	269. 1	122. 2	127. 2	126. 2	125. 8	120. 2	132. 5
240	270. 2	122. 7	127. 8	126. 8	126. 3	120. 7	133. 1
241	271. 3	123. 3	128. 3	127. 4	126. 9	121. 3	133. 7
242	272. 5	123. 8	128. 9	127. 9	127. 5	121. 9	134. 2
243	273. 6	124. 4	129. 5	128. 5	128. 0	122. 5	134. 8
244	274. 7	124. 9	130. 0	129. 1	128. 6	123. 0	135. 4
245	275. 8	125. 5	130. 6	129. 6	129. 2	123. 6	136. 0
246	277. 0	126. 0	131. 2	130. 2	129. 8	124. 2	136. 6
247	278. 1	126. 6	131. 7	130. 8	130. 3	124. 8	137. 2
248	279. 2	127. 1	132. 3	131. 3	130. 9	125. 3	137. 7
249	280. 3	127. 7	132. 9	131. 9	131. 5	125. 9	138. 3
250	281. 5	128. 2	133. 4	132. 5	132. 0	126. 5	138. 9
251	282. 6	128. 8	134. 0	133. 1	132. 6	127. 1	139. 5
252	283. 7	129. 3	134. 6	133. 6	133. 2	127. 6	140. 1
253	284. 8	129. 9	135. 1	134. 2	133. 8	128. 2	140. 7
254	286. 0	130. 4	135. 7	134. 8	134. 3	128. 8	141. 3
255	287. 1	131. 0	136. 3	135. 3	134. 9	129. 4	141. 8
256	288. 2	131. 6	136. 8	135. 9	135. 5	130. 0	142. 4
257	289. 3	132. 1	137. 4	136. 5	136. 0	130. 5	143. 0
258	290. 5	132. 7	138. 0	137. 1	136. 6	131. 1	143. 6
259	291. 6	133. 2	138. 6	137. 6	137. 2	131. 7	144. 2
260	292. 7	133. 8	139. 1	138. 2	137. 8	132. 3	144. 8
261	293. 8	134. 3	139. 7	138. 8	138. 3	132. 9	145. 4
262	295. 0	134. 9	140. 3	139. 4	138. 9	133. 4	145. 9
263	296. 1	135. 4	140. 8	139. 9	139. 5	134. 0	146. 5
264	297. 2	136. 0	141. 4	140. 5	140. 1	134. 6	147. 1
265	298. 3	136. 5	142. 0	141. 1	140. 7	135. 2	147. 7
266	299. 5	137. 1	142. 6	141. 7	141. 2	135. 8	148. 3
267	300. 6	137. 7	143. 1	142. 2	141. 8	136. 3	148. 9
268	301. 7	138. 2	143. 7	142. 8	142. 4	136. 9	149. 5
269	302. 9	138. 8	144. 3	143. 4	143. 0	137. 5	150. 1
270	304. 0	139. 3	144. 8	144. 0	143. 5	138. 1	150. 6
271	305. 1	139. 9	145. 4	144. 5	144. 1	138. 7	151. 2
272	306. 2	140. 4	146. 0	145. 1	144. 7	139. 3	151. 8
273	307. 4	141. 0	146. 6	145. 7	145. 3	139. 8	152. 4
274	308. 5	141. 6	147. 1	146. 3	145. 9	140. 4	153. 0

See footnotes at end of table.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of Straughn and Given					Values of Walker
			Lactose.H_2O and sucrose		
Copper	Cuprous oxide	Lactose.H_2O	1 lactose 4 sucrose	1 lactose 12 sucrose	Maltose.H_2O
mg	*mg*	*mg*	*mg*	*mg*	*mg*
230	258. 9	176. 3	171. 9	156. 1	213. 8
231	260. 1	177. 1	172. 6	156. 8	214. 7
232	261. 2	177. 8	173. 4	157. 5	215. 6
233	262. 3	178. 6	174. 2	158. 2	216. 6
234	263. 4	179. 4	175. 0	158. 9	217. 5
235	264. 6	180. 2	175. 7	159. 6	218. 5
236	265. 7	181. 0	176. 5	160. 3	219. 4
237	266. 8	181. 8	177. 3	161. 0	220. 3
238	268. 0	182. 6	178. 0	161. 7	221. 3
239	269. 1	183. 3	178. 8	162. 4	222. 2
240	270. 2	184. 1	179. 6	163. 1	223. 1
241	271. 3	184. 8	180. 3	163. 8	224. 1
242	272. 5	185. 6	181. 1	164. 5	225. 0
243	273. 6	186. 4	181. 9	165. 2	226. 0
244	274. 7	187. 2	182. 6	165. 9	226. 9
245	275. 8	188. 0	183. 4	166. 7	227. 8
246	277. 0	188. 8	184. 2	167. 4	228. 8
247	278. 1	189. 6	184. 9	168. 1	229. 7
248	279. 2	190. 4	185. 7	168. 8	230. 7
249	280. 3	191. 1	186. 5	169. 5	231. 6
250	281. 5	191. 9	187. 3	170. 2	232. 5
251	282. 6	192. 7	188. 0	170. 9	233. 5
252	283. 7	193. 5	188. 8	171. 6	234. 4
253	284. 8	194. 3	189. 6	172. 3	235. 3
254	286. 0	195. 1	190. 3	173. 0	236. 3
255	287. 1	195. 8	191. 1	173. 7	237. 2
256	288. 2	196. 6	191. 9	174. 4	238. 2
257	289. 3	197. 4	192. 6	175. 1	239. 1
258	290. 5	198. 1	193. 4	175. 8	240. 0
259	291. 6	198. 9	194. 2	176. 5	240. 9
260	292. 7	199. 7	194. 9	177. 2	241. 9
261	293. 8	200. 5	195. 7	178. 0	242. 8
262	295. 0	201. 3	196. 5	178. 7	243. 7
263	296. 1	202. 1	197. 2	179. 4	244. 7
264	297. 2	202. 9	198. 0	180. 1	245. 6
265	298. 3	203. 7	198. 8	180. 8	246. 6
266	299. 5	204. 4	199. 5	181. 5	247. 5
267	300. 6	205. 2	200. 3	182. 2	248. 4
268	301. 7	206. 0	201. 1	182. 9	249. 4
269	302. 9	206. 8	201. 9	183. 6	250. 3
270	304. 0	207. 6	202. 7	184. 4	251. 2
271	305. 1	208. 4	203. 4	185. 1	252. 2
272	306. 2	209. 2	204. 2	185. 8	253. 1
273	307. 4	209. 9	204. 9	186. 5	254. 1
274	308. 5	210. 7	205. 7	187. 2	255. 0

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of National Bureau of Standards (Hammond)

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
275	309. 6	142. 1	147. 7	146. 8	146. 4	141. 0	153. 6
276	310. 7	142. 7	148. 3	147. 4	147. 0	141. 6	154. 2
277	311. 9	143. 2	148. 9	148. 0	147. 6	142. 2	154. 8
278	313. 0	143. 8	149. 4	148. 6	148. 2	142. 8	155. 4
279	314. 1	144. 4	150. 0	149. 2	148. 8	143. 4	156. 0
280	315. 2	144. 9	150. 6	149. 7	149. 3	143. 9	156. 5
281	316. 4	145. 5	151. 2	150. 3	149. 9	144. 5	157. 1
282	317. 5	146. 0	151. 8	150. 9	150. 5	145. 1	157. 7
283	318. 6	146. 6	152. 3	151. 5	151. 1	145. 7	158. 3
284	319. 7	147. 2	152. 9	152. 1	151. 7	146. 3	158. 9
285	320. 9	147. 7	153. 5	152. 6	152. 2	146. 9	159. 5
286	322. 0	148. 3	154. 1	153. 2	152. 8	147. 5	160. 1
287	323. 1	148. 8	154. 6	153. 8	153. 4	148. 1	160. 7
288	324. 2	149. 4	155. 2	154. 4	154. 0	148. 6	161. 3
289	325. 4	150. 0	155. 8	155. 0	154. 6	149. 2	161. 9
290	326. 5	150. 5	156. 4	155. 5	155. 2	149. 8	162. 5
291	327. 6	151. 1	157. 0	156. 1	155. 7	150. 4	163. 1
292	328. 7	151. 7	157. 5	156. 7	156. 3	151. 0	163. 7
293	329. 9	152. 2	158. 1	157. 3	156. 9	151. 6	164. 3
294	331. 0	152. 8	158. 7	157. 9	157. 5	152. 2	164. 9
295	332. 1	153. 4	159. 3	158. 5	158. 1	152. 8	165. 4
296	333. 3	153. 9	159. 9	159. 0	158. 7	153. 4	166. 0
297	334. 4	154. 5	160. 5	159. 6	159. 3	154. 0	166. 6
298	335. 5	155. 1	161. 0	160. 2	159. 9	154. 6	167. 2
299	336. 6	155. 6	161. 6	160. 8	160. 4	155. 2	167. 8
300	337. 8	156. 2	162. 2	161. 4	161. 0	155. 7	168. 4
301	338. 9	156. 8	162. 8	162. 0	161. 6	156. 3	169. 0
302	340. 0	157. 3	163. 4	162. 5	162. 2	156. 9	169. 6
303	341. 1	157. 9	164. 0	163. 1	162. 8	157. 5	170. 2
304	342. 3	158. 5	164. 5	163. 7	163. 4	158. 1	170. 8
305	343. 4	159. 0	165. 1	164. 3	164. 0	158. 7	171. 4
306	344. 5	159. 6	165. 7	164. 9	164. 6	159. 3	172. 0
307	345. 6	160. 2	166. 3	165. 5	165. 1	159. 9	172. 6
308	346. 8	160. 7	166. 9	166. 1	165. 7	160. 5	173. 2
309	347. 9	161. 3	167. 5	166. 7	166. 3	161. 1	173. 8
310	349. 0	161. 9	168. 0	167. 2	166. 9	161. 7	174. 4
311	350. 1	162. 5	168. 6	167. 8	167. 5	162. 3	175. 0
312	351. 3	163. 0	169. 2	168. 4	168. 1	162. 9	175. 6
313	352. 4	163. 6	169. 8	169. 0	168. 7	163. 5	176. 2
314	353. 5	164. 2	170. 4	169. 6	169. 3	164. 1	176. 8
315	354. 6	164. 7	171. 0	170. 2	169. 9	164. 7	177. 4
316	355. 8	165. 3	171. 6	170. 8	170. 5	165. 3	178. 0
317	356. 9	165. 9	172. 2	171. 4	171. 1	165. 9	178. 6
318	358. 0	166. 5	172. 8	172. 0	171. 7	166. 5	179. 2
319	359. 1	167. 0	173. 3	172. 6	172. 2	167. 1	179. 8

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of Straughn and Given					Values of Walker
			Lactose.H_2O and sucrose		
Copper	Cuprous oxide	Lactose.H_2O	1 lactose 4 sucrose	1 lactose 12 sucrose	Maltose.H_2O
mg	*mg*	*mg*	*mg*	*mg*	*mg*
275	309. 6	211. 5	206. 5	187. 9	255. 9
276	310. 7	212. 3	207. 3	188. 6	256. 9
277	311. 9	213. 1	208. 1	189. 3	257. 8
278	313. 0	213. 9	208. 8	190. 0	258. 8
279	314. 1	214. 7	209. 6	190. 7	259. 7
280	315. 2	215. 5	210. 4	191. 4	260. 6
281	316. 4	216. 2	211. 1	192. 1	261. 5
282	317. 5	217. 0	211. 9	192. 9	262. 5
283	318. 6	217. 7	212. 7	193. 6	263. 4
284	319. 7	218. 5	213. 4	194. 3	264. 4
285	320. 9	219. 3	214. 2	195. 0	265. 3
286	322. 0	220. 1	215. 0	195. 7	266. 2
287	323. 1	220. 9	215. 8	196. 4	267. 2
288	324. 2	221. 7	216. 5	197. 1	268. 1
289	325. 4	222. 5	217. 3	197. 8	269. 0
290	326. 5	223. 3	218. 1	198. 6	270. 0
291	327. 6	224. 0	218. 8	199. 3	270. 9
292	328. 7	224. 8	219. 6	200. 0	271. 9
293	329. 9	225. 6	220. 4	200. 7	272. 8
294	331. 0	226. 4	221. 2	201. 4	273. 7
295	332. 1	227. 2	221. 9	202. 1	274. 7
296	333. 3	228. 0	222. 7	202. 8	275. 6
297	334. 4	228. 8	223. 5	203. 6	276. 5
298	335. 5	229. 6	224. 3	204. 3	277. 5
299	336. 6	230. 3	225. 0	205. 0	278. 4
300	337. 8	231. 1	225. 8	205. 7	279. 3
301	338. 9	231. 9	226. 6	206. 4	280. 3
302	340. 0	232. 7	227. 4	207. 1	281. 2
303	341. 1	233. 5	228. 2	207. 8	282. 1
304	342. 3	234. 3	228. 9	208. 5	283. 1
305	343. 4	235. 1	229. 7	209. 3	284. 0
306	344. 5	235. 9	230. 5	210. 0	284. 9
307	345. 6	236. 6	231. 2	210. 7	285. 9
308	346. 8	237. 4	232. 0	211. 5	286. 8
309	347. 9	238. 2	232. 8	212. 2	287. 8
310	349. 0	239. 0	233. 6	212. 9	288. 7
311	350. 1	239. 8	234. 4	213. 6	289. 6
312	351. 3	240. 6	235. 1	214. 3	290. 6
313	352. 4	241. 4	235. 9	215. 0	291. 5
314	353. 5	242. 2	236. 7	215. 7	292. 4
315	354. 6	242. 9	237. 4	216. 5	293. 4
316	355. 8	243. 7	238. 2	217. 2	294. 3
317	356. 9	244. 5	239. 0	217. 9	295. 2
318	358. 0	245. 3	239. 8	218. 6	296. 2
319	359. 1	246. 1	240. 6	219. 3	297. 1

See footnotes at end of table.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of National Bureau of Standards (Hammond)

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
320	360. 3	167. 6	173. 9	173. 1	172. 8	167. 7	180. 4
321	361. 4	168. 2	174. 5	173. 7	173. 4	168. 3	181. 0
322	362. 5	168. 8	175. 1	174. 3	174. 0	168. 9	181. 6
323	363. 6	169. 3	175. 7	174. 9	174. 6	169. 5	182. 2
324	364. 8	169. 9	176. 3	175. 5	175. 2	170. 1	182. 8
325	365. 9	170. 5	176. 9	176. 1	175. 8	170. 7	183. 4
326	367. 0	171. 1	177. 5	176. 7	176. 4	171. 3	184. 0
327	368. 2	171. 6	178. 1	177. 3	177. 0	171. 9	184. 6
328	369. 3	172. 2	178. 7	177. 9	177. 6	172. 5	185. 2
329	370. 4	172. 8	179. 2	178. 5	178. 2	173. 1	185. 8
330	371. 5	173. 4	179. 8	179. 1	178. 8	173. 7	186. 4
331	372. 7	173. 9	180. 4	179. 7	179. 4	174. 3	187. 0
332	373. 8	174. 5	181. 0	180. 3	180. 0	174. 9	187. 6
333	374. 9	175. 1	181. 6	180. 9	180. 6	175. 5	188. 2
334	376. 0	175. 7	182. 2	181. 5	181. 2	176. 1	188. 8
335	377. 2	176. 3	182. 8	182. 1	181. 8	176. 7	189. 4
336	378. 3	176. 8	183. 4	182. 6	182. 4	177. 3	190. 1
337	379. 4	177. 4	184. 0	183. 2	183. 0	178. 0	190. 7
338	380. 5	178. 0	184. 6	183. 8	183. 6	178. 6	191. 3
339	381. 7	178. 6	185. 2	184. 4	184. 2	179. 2	191. 9
340	382. 8	179. 2	185. 8	185. 0	184. 8	179. 8	192. 5
341	383. 9	179. 7	186. 4	185. 6	185. 4	180. 4	193. 1
342	385. 0	180. 3	187. 0	186. 2	186. 0	181. 0	193. 7
343	386. 2	180. 9	187. 6	186. 8	186. 6	181. 6	194. 3
344	387. 3	181. 5	188. 2	187. 4	187. 2	182. 2	194. 9
345	388. 4	182. 1	188. 8	188. 0	187. 8	182. 8	195. 5
346	389. 5	182. 7	189. 4	188. 6	188. 4	183. 4	196. 1
347	390. 7	183. 2	190. 0	189. 2	189. 0	184. 0	196. 7
348	391. 8	183. 8	190. 6	189. 8	189. 6	184. 6	197. 3
349	392. 9	184. 4	191. 2	190. 4	190. 2	185. 3	197. 9
350	394. 0	185. 0	191. 8	191. 0	190. 8	185. 9	198. 5
351	395. 2	185. 6	192. 4	191. 6	191. 4	186. 5	199. 2
352	396. 3	186. 2	193. 0	192. 2	192. 0	187. 1	199. 8
353	397. 4	186. 8	193. 6	192. 8	192. 6	187. 7	200. 4
354	398. 5	187. 3	194. 2	193. 4	193. 2	188. 3	201. 0
355	399. 7	187. 9	194. 8	194. 0	193. 8	188. 9	201. 6
356	400. 8	188. 5	195. 4	194. 6	194. 4	189. 5	202. 2
357	401. 9	189. 1	196. 0	195. 2	195. 0	190. 2	202. 8
358	403. 1	189. 7	196. 6	195. 8	195. 7	190. 8	203. 4
359	404. 2	190. 3	197. 2	196. 4	196. 3	191. 4	204. 0
360	405. 3	190. 9	197. 8	197. 1	196. 9	192. 0	204. 7
361	406. 4	191. 5	198. 4	197. 7	197. 5	192. 6	205. 3
362	407. 6	192. 0	199. 0	198. 3	198. 1	193. 2	205. 9
363	408. 7	192. 6	199. 6	198. 9	198. 7	193. 9	206. 5
364	409. 8	193. 2	200. 2	199. 5	199. 3	194. 5	207. 1

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of Straughn and Given					Values of Walker
			Lactose.H_2O and sucrose		
Copper	Cuprous oxide	Lactose.H_2O	1 lactose 4 sucrose	1 lactose 12 sucrose	Maltose.H_2O
mg	*mg*	*mg*	*mg*	*mg*	*mg*
320	360. 3	246. 9	241. 4	220. 1	298. 0
321	361. 4	247. 7	242. 1	220. 8	299. 0
322	362. 5	248. 5	242. 9	221. 5	299. 9
323	363. 6	249. 3	243. 7	222. 2	300. 9
324	364. 8	250. 1	244. 4	222. 9	301. 8
325	365. 9	250. 9	245. 2	223. 7	302. 7
326	367. 0	251. 6	246. 0	224. 4	303. 6
327	368. 2	252. 4	246. 8	225. 1	304. 6
328	369. 3	253. 2	247. 6	225. 8	305. 5
329	370. 4	254. 0	248. 4	226. 6	306. 5
330	371. 5	254. 8	249. 2	227. 3	307. 4
331	372. 7	255. 6	250. 0	228. 0	308. 3
332	373. 8	256. 4	250. 7	228. 8	309. 3
333	374. 9	257. 1	251. 5	229. 5	310. 2
334	376. 0	257. 9	252. 3	230. 2	311. 2
335	377. 2	258. 7	253. 0	230. 9	312. 1
336	378. 3	259. 5	253. 8	231. 7	313. 0
337	379. 4	260. 3	254. 6	232. 4	314. 0
338	380. 5	261. 1	255. 4	233. 1	314. 9
339	381. 7	261. 9	256. 2	233. 8	315. 8
340	382. 8	262. 7	257. 0	234. 6	316. 8
341	383. 9	263. 4	257. 7	235. 3	317. 7
342	385. 0	264. 2	258. 5	236. 0	318. 6
343	386. 2	265. 0	259. 3	236. 7	319. 6
344	387. 3	265. 8	260. 0	237. 5	320. 5
345	388. 4	266. 6	260. 8	238. 2	321. 4
346	389. 5	267. 4	261. 6	238. 9	322. 4
347	390. 7	268. 2	262. 4	239. 7	323. 3
348	391. 8	269. 0	263. 2	240. 4	324. 3
349	392. 9	269. 7	263. 9	241. 1	325. 2
350	394. 0	270. 5	264. 7	241. 9	326. 1
351	395. 2	271. 3	265. 5	242. 6	327. 0
352	396. 3	272. 1	266. 3	243. 3	328. 0
353	397. 4	272. 9	267. 1	244. 1	328. 9
354	398. 5	273. 7	267. 9	244. 8	329. 9
355	399. 7	274. 5	268. 7	245. 5	330. 8
356	400. 8	275. 3	269. 5	246. 2	331. 7
357	401. 9	276. 0	270. 2	247. 0	332. 7
358	403. 1	276. 8	271. 0	247. 7	333. 6
359	404. 2	277. 6	271. 8	248. 4	334. 5
360	405. 3	278. 4	272. 5	249. 2	335. 5
361	406. 4	279. 2	273. 3	249. 9	336. 4
362	407. 6	280. 0	274. 1	250. 7	337. 3
363	408. 7	280. 8	274. 9	251. 4	338. 3
364	409. 8	281. 6	275. 7	252. 1	339. 2

See footnotes at end of table.

TABLE 78.—*Reducing-sugar values by the Munson anh Walker method*—Continued

Values of National Bureau of Standards (Hammond)

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
365	410. 9	193. 8	200. 8	200. 1	199. 9	195. 1	207. 7
366	412. 1	194. 4	201. 4	200. 7	200. 5	195. 7	208. 3
367	413. 2	195. 0	202. 0	201. 3	201. 1	196. 3	209. 0
368	414. 3	195. 6	202. 6	201. 9	201. 7	196. 9	209. 6
369	415. 4	196. 2	203. 2	202. 5	202. 4	197. 6	210. 2
370	416. 6	196. 8	203. 8	203. 1	203. 0	198. 2	210. 8
371	417. 7	197. 4	204. 4	203. 7	203. 6	198. 8	211. 4
372	418. 8	198. 0	205. 0	204. 3	204. 2	199. 4	212. 0
373	419. 9	198. 5	205. 7	204. 9	204. 8	200. 0	212. 6
374	421. 1	199. 1	206. 3	205. 6	205. 4	200. 7	213. 3
375	422. 2	199. 7	206. 9	206. 2	206. 0	201. 3	213. 9
376	423. 3	200. 3	207. 5	206. 8	206. 6	201. 9	214. 5
377	424. 4	200. 9	208. 1	207. 4	207. 3	202. 5	215. 1
378	425. 6	201. 5	208. 7	208. 0	207. 9	203. 1	215. 7
379	426. 7	202. 1	209. 3	208. 6	208. 5	203. 8	216. 3
380	427. 8	202. 7	209. 9	209. 2	209. 1	204. 4	217. 0
381	428. 9	203. 3	210. 5	209. 8	209. 7	205. 0	217. 6
382	430. 1	203. 9	211. 1	210. 4	210. 3	205. 6	218. 2
383	431. 2	204. 5	211. 8	211. 1	211. 0	206. 3	218. 8
384	432. 3	205. 1	212. 4	211. 7	211. 6	206. 9	219. 5
385	433. 5	205. 7	213. 0	212. 3	212. 2	207. 5	220. 1
386	434. 6	206. 3	213. 6	212. 9	212. 8	208. 1	220. 7
387	435. 7	206. 9	214. 2	213. 5	213. 4	208. 8	221. 3
388	436. 8	207. 5	214. 8	214. 1	214. 0	209. 4	221. 9
389	438. 0	208. 1	215. 4	214. 7	214. 7	210. 0	222. 6
390	439. 1	208. 7	216. 0	215. 4	215. 3	210. 6	223. 2
391	440. 2	209. 3	216. 7	216. 0	215. 9	211. 3	223. 8
392	441. 3	209. 9	217. 3	216. 6	216. 5	211. 9	224. 4
393	442. 5	210. 5	217. 9	217. 2	217. 1	212. 5	225. 1
394	443. 6	211. 1	218. 5	217. 8	217. 8	213. 2	225. 7
395	444. 7	211. 7	219. 1	218. 5	218. 4	213. 8	226. 3
396	445. 8	212. 3	219. 8	219. 1	219. 0	214. 4	226. 9
397	447. 0	212. 9	220. 4	219. 7	219. 6	215. 1	227. 6
398	448. 1	213. 5	221. 0	220. 3	220. 3	215. 7	228. 2
399	449. 2	214. 1	221. 6	220. 9	220. 9	216. 3	228. 8
400	450. 3	214. 7	222. 2	221. 5	221. 5	217. 0	229. 4
401	451. 5	215. 3	222. 9	222. 2	222. 1	217. 6	230. 1
402	452. 6	215. 9	223. 5	222. 8	222. 8	218. 2	230. 7
403	453. 7	216. 5	224. 1	223. 4	223. 4	218. 9	231. 3
404	454. 8	217. 1	224. 7	224. 0	224. 0	219. 5	232. 0
405	456. 0	217. 8	225. 4	224. 7	224. 7	220. 1	232. 6
406	457. 1	218. 4	226. 0	225. 3	225. 3	220. 8	233. 2
407	458. 2	219. 0	226. 6	225. 9	225. 9	221. 4	233. 9
408	459. 3	219. 6	227. 2	226. 6	226. 5	222. 0	234. 5
409	460. 5	220. 2	227. 9	227. 2	227. 2	222. 7	235. 1

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of Straughn and Given					Values of Walker
			Lactose.H_2O and sucrose		
Copper	Cuprous oxide	Lactose.H_2O	1 lactose 4 sucrose	1 lactose 12 sucrose	Maltose.H_2O
mg	*mg*	*mg*	*mg*	*mg*	*mg*
365	410. 9	282. 4	276. 5	252. 9	340. 2
366	412. 1	283. 2	277. 3	253. 6	341. 1
367	413. 2	284. 0	278. 0	254. 3	342. 0
368	414. 3	284. 8	278. 8	255. 1	343. 0
369	415. 4	285. 6	279. 6	255. 8	343. 9
370	416. 6	286. 4	280. 4	256. 5	344. 8
371	417. 7	287. 2	281. 2	257. 3	345. 8
372	418. 8	288. 0	282. 0	258. 0	346. 7
373	419. 9	288. 8	282. 8	258. 7	347. 6
374	421. 1	289. 5	283. 5	259. 5	348. 5
375	422. 2	290. 3	284. 3	260. 2	349. 5
376	423. 3	291. 1	285. 1	260. 9	350. 5
377	424. 4	291. 9	285. 9	261. 7	351. 4
378	425. 6	292. 7	286. 7	262. 4	352. 3
379	426. 7	293. 5	287. 5	263. 2	353. 2
380	427. 8	294. 3	288. 3	263. 9	354. 2
381	428. 9	295. 1	289. 1	264. 6	355. 1
382	430. 1	295. 8	289. 8	265. 4	356. 0
383	431. 2	296. 6	290. 6	266. 1	357. 0
384	432. 3	297. 4	291. 4	266. 9	357. 9
385	433. 5	298. 2	292. 2	267. 6	358. 9
386	434. 6	299. 0	293. 0	268. 4	359. 8
387	435. 7	299. 8	293. 8	269. 1	360. 7
388	436. 8	300. 6	294. 6	269. 9	361. 7
389	438. 0	301. 4	295. 4	270. 6	362. 6
390	439. 1	302. 1	296. 1	271. 3	363. 5
391	440. 2	302. 9	296. 9	272. 1	364. 5
392	441. 3	303. 7	297. 7	272. 8	365. 4
393	442. 5	304. 5	298. 5	273. 6	366. 3
394	443. 6	305. 3	299. 3	274. 3	367. 3
395	444. 7	306. 1	300. 1	275. 1	368. 2
396	445. 8	306. 9	300. 9	275. 8	369. 1
397	447. 0	307. 7	301. 7	276. 6	370. 1
398	448. 1	308. 5	302. 5	277. 3	371. 0
399	449. 2	309. 3	303. 2	278. 1	371. 9
400	450. 3	310. 1	304. 0	278. 8	372. 9
401	451. 5	310. 9	304. 8	279. 5	373. 8
402	452. 6	311. 7	305. 6	280. 3	374. 7
403	453. 7	312. 5	306. 4	281. 0	375. 7
404	454. 8	313. 3	307. 2	281. 8	376. 6
405	456. 0	314. 1	308. 0	282. 5	377. 6
406	457. 1	314. 9	308. 8	283. 2	378. 5
407	458. 2	315. 7	309. 5	284. 0	379. 4
408	459. 3	316. 4	310. 3	284. 8	380. 3
409	460. 5	317. 2	311. 1	285. 5	381. 3

See footnotes at end of table.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of National Bureau of Standards (Hammond)

Copper	Cuprous oxide	Dextrose	Invert sugar	Invert sugar and sucrose			Levulose
				0.3 g of total sugar	0.4 g of total sugar	2.0 g of total sugar	
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
410	461. 6	220. 8	228. 5	227. 8	227. 8	223. 3	235. 8
411	462. 7	221. 4	229. 1	228. 4	228. 4	224. 0	236. 4
412	463. 8	222. 0	229. 7	229. 1	229. 1	224. 6	237. 1
413	465. 0	222. 6	230. 4	229. 7	229. 7	225. 3	237. 7
414	466. 1	223. 3	231. 0	230. 4	230. 4	225. 9	238. 4
415	467. 2	223. 9	231. 7	231. 0	231. 0	226. 6	239. 0
416	468. 4	224. 5	232. 3	231. 6	231. 7	227. 2	239. 7
417	469. 5	225. 1	232. 9	232. 3	232. 3	227. 8	240. 3
418	470. 6	225. 7	233. 6	232. 9	232. 9	228. 5	241. 0
419	471. 7	226. 3	234. 2	233. 5	233. 6	229. 1	241. 6
420	472. 9	227. 0	234. 8	234. 2	234. 2	229. 8	242. 2
421	474. 0	227. 6	235. 5	234. 8	234. 9	230. 4	242. 9
422	475. 1	228. 2	236. 1	235. 5	235. 5	231. 1	243. 6
423	476. 2	228. 8	236. 8	236. 2	236. 2	231. 8	244. 3
424	477. 4	229. 5	237. 5	236. 8	236. 9	232. 4	244. 9
425	478. 5	230. 1	238. 1	237. 5	237. 5	233. 1	245. 6
426	479. 6	230. 7	238. 8	238. 2	238. 2	233. 8	246. 3
427	480. 7	231. 4	239. 5	238. 8	238. 9	234. 5	247. 0
428	481. 9	232. 0	240. 2	239. 5	239. 6	235. 1	247. 8
429	483. 0	232. 7	240. 8	240. 2	240. 3	235. 8	248. 5
430	484. 1	233. 3	241. 5	240. 9	241. 0	236. 5	249. 2
431	485. 2	234. 0	242. 3	241. 7	241. 7	237. 2	250. 0
432	486. 4	234. 7	243. 0	242. 4	242. 5	238. 0	250. 8
433	487. 5	235. 3	243. 8	243. 2	243. 3	238. 7	251. 6
434	488. 6	236. 1	244. 7	244. 1	244. 2	239. 6	252. 7
435	489. 7	236. 9	245. 6	245. 1	245. 1	240. 4	253. 7

[1] L. S. Munson and P. H. Walker, J. Am. Chem. Soc. **28**, 663 (1906).
[2] L. D. Hammond, J. Research NBS **24**, 589 (1940) RP1301.

TABLE 78.—*Reducing-sugar values by the Munson and Walker method*—Continued

Values of Straughn and Given					Values of Walker
Copper	Cuprous oxide	Lactose.H_2O	Lactose.H_2O and sucrose		Maltose.H_2O
			1 lactose 4 sucrose	1 lactose 12 sucrose	
mg	*mg*	*mg*	*mg*	*mg*	*mg*
410	461. 6	318. 0	311. 9	286. 2	382. 2
411	462. 7	318. 8	312. 7	287. 0	383. 1
412	463. 8	319. 6	313. 5	287. 8	384. 1
413	465. 0	320. 4	314. 3	288. 5	385. 0
414	466. 1	321. 1	315. 1	289. 2	386. 0
415	467. 2	321. 9	315. 8	290. 0	386. 9
416	468. 4	322. 7	316. 6	290. 8	387. 8
417	469. 5	323. 5	317. 4	291. 5	388. 7
418	470. 6	324. 3	318. 1	292. 2	389. 7
419	471. 7	325. 1	318. 9	293. 0	390. 6
420	472. 9	325. 9	319. 7	293. 7	391. 6
421	474. 0	326. 7	320. 5	294. 5	392. 5
422	475. 1	327. 5	321. 3	295. 2	393. 4
423	476. 2	328. 3	322. 1	296. 0	394. 4
424	477. 4	329. 1	322. 8	296. 7	395. 3
425	478. 5	329. 9	323. 6	297. 5	396. 2
426	479. 6	330. 7	324. 4	298. 2	397. 1
427	480. 7	331. 5	325. 2	299. 0	398. 1
428	481. 9	332. 3	326. 0	299. 7	399. 0
429	483. 0	333. 1	326. 8	300. 4	400. 0
430	484. 1	333. 9	327. 6	301. 2	400. 9
431	485. 2	334. 7	328. 4	302. 0	401. 8
432	486. 4	335. 5	329. 2	302. 7	402. 7
433	487. 5	336. 2	330. 0	303. 5	403. 7
434	488. 6	337. 0	330. 7	304. 2	404. 6
435	489. 7	337. 8	331. 5	305. 0	405. 6

[3] A. Given, Methods for Sugar Analysis (P. Blakiston's Sons & Co., Philadelphia, Pa., 1912).

[4] P. H. Walker, J. Am. Chem. Soc. **29**, 541 (1907).

[5] The values in the table for concentrations of reducing sugar less than 20 mg are extrapolated and should be used with caution and only for approximate determinations.

TABLE 79.—*Allihn table for the determination of dextrose*

Copper	Cuprous oxide	Dextrose	Copper	Cuprous oxide	Dextrose	Copper	Cuprous oxide	Dextrose	Copper	Cuprous oxide	Dextrose
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
11	12.4	6.6	76	85.6	38.8	141	158.7	71.8	206	231.9	105.8
12	13.5	7.1	77	86.7	39.3	142	159.9	72.3	207	233.0	106.3
13	14.6	7.6	78	87.8	39.8	143	161.0	72.9	208	234.2	106.4
14	15.8	8.1	79	88.9	40.3	144	162.1	73.4	209	235.3	107.9
15	16.9	8.6	80	90.1	40.8	145	163.2	73.9	210	236.4	107.8
16	18.0	9.0	81	91.2	41.3	146	164.4	74.4	211	237.6	108.4
17	19.1	9.5	82	92.3	41.8	147	165.5	74.9	212	238.7	109.0
18	20.3	10.0	83	93.4	42.3	148	166.6	75.5	213	239.8	109.5
19	21.4	10.5	84	94.6	42.8	149	167.7	76.0	214	240.9	110.0
20	22.5	11.0	85	95.7	43.4	150	168.9	76.5	215	242.1	110.6
21	23.6	11.5	86	96.8	43.9	151	170.0	77.0	216	243.2	111.1
22	24.8	12.0	87	97.9	44.4	152	171.1	77.5	217	244.3	111.6
23	25.9	12.5	88	99.1	44.9	153	172.3	78.1	218	245.4	112.1
24	27.0	13.0	89	100.2	45.4	154	173.4	78.6	219	246.6	112.7
25	28.1	13.5	90	101.3	45.9	155	174.5	79.1	220	247.7	113.2
26	29.3	14.0	91	102.4	46.4	156	175.6	79.6	221	248.7	113.7
27	30.4	14.5	92	103.6	46.9	157	176.8	80.1	222	249.9	114.3
28	31.5	15.0	93	104.7	47.4	158	177.9	80.7	223	251.0	114.8
29	32.7	15.5	94	105.8	47.9	159	179.0	81.2	224	252.4	115.3
30	33.8	16.0	95	107.0	48.4	160	180.1	81.7	225	253.3	115.9
31	34.9	16.5	96	108.1	48.9	161	181.3	82.2	226	254.4	116.4
32	36.0	17.0	97	109.2	49.4	162	182.4	82.7	227	255.6	116.9
33	37.2	17.5	98	110.3	49.9	163	183.5	83.3	228	256.7	117.4
34	38.3	18.0	99	111.5	50.4	164	184.6	83.8	229	257.8	118.0
35	39.4	18.5	100	112.6	50.9	165	185.8	84.3	230	258.9	118.5
36	40.5	18.9	101	113.7	51.4	166	186.9	84.8	231	260.1	119.0
37	41.7	19.4	102	114.8	51.9	167	188.0	85.3	232	261.2	119.6
38	42.8	19.9	103	116.0	52.4	168	189.1	85.9	233	262.3	120.1
39	43.9	20.4	104	117.1	52.9	169	190.3	86.4	234	263.4	120.7
40	45.0	20.9	105	118.2	53.5	170	191.4	86.9	235	264.6	121.2
41	46.2	21.4	106	119.3	54.0	171	192.5	87.4	236	265.7	121.7
42	47.3	21.9	107	120.5	54.5	172	193.6	87.9	237	266.8	122.3
43	48.4	22.4	108	121.6	55.0	173	194.8	88.5	238	268.0	122.8
44	49.5	22.9	109	122.7	55.5	174	195.9	89.0	239	269.1	123.4
45	50.7	23.4	110	123.8	56.0	175	197.0	89.5	240	270.2	123.9
46	51.8	23.9	111	125.0	56.5	176	198.1	90.0	241	271.3	124.4
47	52.9	24.4	112	126.1	57.0	177	199.3	90.5	242	272.5	125.0
48	54.0	24.9	113	127.2	57.5	178	200.4	91.1	243	273.6	125.5
49	55.2	25.4	114	128.3	58.0	179	201.5	91.6	244	274.7	126.0
50	56.3	25.9	115	129.6	58.6	180	202.6	92.1	245	275.8	126.6
51	57.4	26.4	116	130.6	59.1	181	203.8	92.6	246	277.0	127.1
52	58.5	26.9	117	131.7	59.6	182	204.9	93.1	247	278.1	127.6
53	59.7	27.4	118	132.8	60.1	183	206.0	93.7	248	279.2	128.1
54	60.8	27.9	119	134.0	60.6	184	207.1	94.2	249	280.3	128.7
55	61.9	28.4	120	135.1	61.1	185	208.3	94.7	250	281.5	129.2
56	63.0	28.8	121	136.2	61.6	186	209.4	95.2	251	282.6	129.7
57	64.2	29.3	122	137.4	62.1	187	210.5	95.7	252	283.7	130.3
58	65.3	29.8	123	138.5	62.6	188	211.7	96.3	253	284.8	130.8
59	66.4	30.3	124	139.6	63.1	189	212.8	96.8	254	286.0	131.4
60	67.6	30.8	125	140.7	63.7	190	213.9	97.3	255	287.1	131.9
61	68.7	31.3	126	141.9	64.2	191	215.0	97.8	256	288.2	132.4
62	69.8	31.8	127	143.0	64.7	192	216.2	98.4	257	289.3	133.0
63	70.9	32.3	128	144.1	65.2	193	217.3	98.9	258	290.5	133.5
64	72.1	32.8	129	145.2	65.7	194	218.4	99.4	259	291.6	134.1
65	73.2	33.3	130	146.4	66.2	195	219.5	100.0	260	292.7	134.6
66	74.3	33.8	131	147.5	66.7	196	220.7	100.5	261	293.8	135.1
67	75.4	34.3	132	148.6	67.2	197	221.8	101.0	262	295.0	135.7
68	76.6	34.8	133	149.7	67.7	198	222.9	101.5	623	296.1	136.2
69	77.7	35.3	134	150.9	68.2	199	224.0	102.0	264	297.2	136.8
70	78.8	35.8	135	152.0	68.8	200	225.2	102.6	265	298.3	137.3
71	79.9	36.3	136	153.1	69.3	201	226.3	103.1	266	299.5	137.8
72	81.1	36.8	137	154.2	69.8	202	227.4	103.7	267	300.6	138.4
73	82.2	37.3	138	155.4	70.3	203	228.5	104.2	268	301.7	138.9
74	83.3	37.8	139	156.5	70.8	204	229.7	104.7	269	302.8	139.5
75	84.4	38.3	140	157.6	71.3	205	230.8	105.3	270	304.0	140.0

TABLE 79.—*Allihn table for the determination of dextrose*—Continued

Copper	Cuprous oxide	Dextrose	Copper	Cuprous oxide	Dextrose	Copper	Cuprous oxide	Dextrose	Copper	Cuprous oxide	Dextrose
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
271	305.1	140.6	320	360.3	167.5	369	415.4	195.1	418	470.6	223.3
272	306.2	141.1	321	361.4	168.1	370	416.6	195.7	419	471.8	223.9
273	307.3	141.7	322	362.5	168.6	371	417.7	196.3	420	472.9	224.5
274	308.5	142.2	323	363.7	169.2	372	418.8	196.8	421	474.0	225.1
275	309.6	142.8	324	364.8	169.7	373	420.0	197.4	422	475.6	225.7
276	310.7	143.3	325	365.9	170.3	374	421.1	198.0	423	476.2	226.3
277	311.9	143.9	326	367.0	170.9	375	422.2	198.6	424	477.4	226.9
278	313.0	144.4	327	368.2	171.4	376	423.3	199.1	425	478.5	227.5
279	314.1	145.0	328	369.3	172.0	377	424.5	199.7	426	479.6	228.0
280	315.2	145.5	329	370.4	172.5	378	425.6	200.3	427	480.7	228.6
281	316.4	146.1	330	371.5	173.1	379	426.7	200.8	428	481.9	229.2
282	317.5	146.6	331	372.7	173.7	380	427.8	201.4	429	483.0	229.8
283	318.6	147.2	332	373.8	174.2	381	429.0	202.0	430	484.1	230.4
284	319.7	147.7	333	374.9	174.8	382	430.1	202.5	431	485.3	231.0
285	320.9	148.3	334	376.0	175.3	383	431.2	203.1	432	486.4	231.6
286	322.0	148.8	335	377.2	175.9	384	432.3	203.7	433	487.5	232.2
287	323.1	149.4	336	378.3	176.5	385	433.5	204.3	434	488.6	232.8
288	324.2	149.9	337	379.4	177.0	386	434.6	204.8	435	489.7	233.4
289	325.4	150.5	338	380.5	177.6	387	435.7	205.4	436	490.9	233.9
290	326.5	151.0	339	381.7	178.1	388	436.8	206.0	437	492.0	234.5
291	327.4	151.6	340	382.8	178.7	389	438.0	206.5	438	493.1	235.1
292	328.7	152.1	341	383.9	179.3	390	439.1	207.1	439	494.3	235.7
293	329.9	152.7	342	385.0	179.8	391	440.2	207.7	440	495.4	236.3
294	331.0	153.2	343	386.2	180.4	392	441.3	208.3	441	496.5	236.9
295	332.1	153.8	344	387.3	180.9	393	442.4	208.8	442	497.6	237.5
296	333.3	154.3	345	388.4	181.5	394	443.6	209.4	443	498.8	238.1
297	334.4	154.9	346	389.6	182.1	395	444.7	210.0	444	499.9	238.7
298	335.5	155.4	347	390.7	182.6	396	445.9	210.6	445	501.0	239.3
299	336.6	156.0	348	391.8	183.2	397	447.0	211.2	446	502.1	239.8
300	337.8	156.5	349	392.9	183.7	398	448.1	211.7	447	503.2	240.4
301	338.9	157.1	350	394.0	184.3	399	449.2	212.3	448	504.4	241.0
302	340.0	157.6	351	395.2	184.9	400	450.3	212.9	449	505.5	241.6
303	341.1	158.2	352	396.3	185.4	401	451.5	213.5	450	506.6	242.2
304	342.3	158.7	353	397.4	186.0	402	452.6	214.1	451	507.8	242.8
			354	398.6	186.6	403	453.7	214.6	452	508.9	243.4
305	343.4	159.3									
306	344.5	159.8	355	399.7	187.2	404	454.8	215.2	453	510.0	244.0
307	345.6	160.4	356	400.8	187.7	405	456.0	215.8	454	511.1	244.6
308	346.8	160.9	357	401.9	188.3	406	457.1	216.4	455	512.3	245.2
309	347.9	161.5	358	403.1	188.9	407	458.2	217.0	456	513.4	245.7
						408	459.4	217.5	457	514.5	246.3
310	349.0	162.0	359	404.2	189.4						
311	350.1	162.6	360	405.3	190.0	409	460.5	218.1	458	515.6	246.9
312	351.3	163.1	361	406.4	190.6	410	461.6	218.7	459	516.8	247.5
313	352.4	163.7	362	407.6	191.1	411	462.7	219.3	460	517.9	248.1
314	353.5	164.2	363	408.7	191.7	412	463.8	219.9	461	519.0	248.7
									462	520.1	249.3
315	354.6	164.8	364	409.8	192.3	413	465.0	220.4			
316	355.8	165.3	365	410.9	192.9	414	466.1	221.0	463	521.3	249.9
317	356.9	165.9	366	412.1	193.4	415	467.2	221.6			
318	358.0	166.4	367	413.2	194.0	416	468.4	222.2			
319	359.1	167.0	368	414.3	194.6	417	469.5	222.8			

TABLE 80.—*Calculation of dextrose, levulose, invert sugar, lactose, and maltose (Ouisumbing and Thomas copper equivalents)*

Copper	Cuprous oxide	Dextrose	Levulose	Invert sugar	Lactose		Maltose	
					$C_{12}H_{22}O_{11}$	$C_{12}H_{22}O_{11}.H_2O$	$C_{12}H_{22}O_{11}$	$C_{12}H_{22}O_{11}.H_2O$
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
10	11. 3	4. 8	5. 3	5. 0	7. 7	8. 1	9. 4	9. 9
20	22. 5	9. 5	10. 5	10. 1	15. 5	16. 3	18. 8	19. 8
30	33. 8	14. 3	15. 8	15. 2	23. 2	24. 4	28. 2	29. 7
40	45. 0	19. 1	21. 2	20. 3	30. 9	32. 5	37. 6	39. 6
50	56. 3	24. 0	26. 5	25. 4	38. 7	40. 7	47. 0	49. 5
60	67. 6	28. 9	31. 9	30. 6	46. 4	48. 8	56. 4	59. 4
70	78. 8	33. 7	37. 2	35. 7	54. 0	56. 9	65. 8	69. 3
80	90. 1	38. 7	42. 6	40. 9	61. 7	65. 0	75. 2	79. 2
90	101. 3	43. 6	48. 0	46. 1	69. 5	73. 2	84. 6	89. 1
100	112. 6	48. 6	53. 4	51. 3	77. 2	81. 3	94. 0	99. 0
110	123. 8	53. 5	58. 8	56. 5	85. 0	89. 5	103. 4	108. 9
120	135. 1	58. 5	64. 3	61. 8	92. 7	97. 6	112. 8	118. 8
130	146. 4	63. 6	70. 7	67. 0	100. 4	105. 7	122. 2	128. 7
140	157. 6	68. 6	75. 2	72. 3	108. 2	113. 9	131. 6	138. 6
150	168. 9	73. 7	80. 7	77. 6	116. 0	122. 0	141. 0	148. 5
160	180. 1	78. 8	86. 2	82. 9	123. 7	130. 1	150. 4	158. 4
170	191. 4	83. 9	91. 7	88. 3	131. 4	138. 3	159. 8	168. 3
180	202. 6	89. 1	97. 2	93. 7	139. 1	146. 4	169. 2	178. 2
190	213. 9	94. 2	102. 8	99. 1	146. 9	154. 6	178. 8	188. 1
200	225. 2	99. 4	108. 4	104. 4	154. 6	162. 7	188. 2	198. 0
210	236. 4	104. 6	114. 0	109. 8	162. 3	170. 9	197. 6	207. 9
220	247. 7	109. 9	119. 6	115. 2	170. 0	179. 0	207. 0	217. 8
230	258. 9	115. 1	125. 2	120. 6	177. 8	187. 2	216. 4	227. 7
240	270. 2	120. 4	130. 8	126. 1	185. 5	195. 3	225. 8	237. 6
250	281. 5	125. 7	136. 4	131. 6	193. 2	203. 4	235. 2	247. 5
260	292. 7	131. 0	142. 1	137. 1	201. 0	211. 6	244. 6	257. 4
270	304. 0	136. 4	147. 8	142. 6	208. 8	219. 8	254. 0	267. 3
280	315. 2	141. 7	153. 5	148. 2	216. 5	227. 9	263. 4	277. 2
290	326. 5	147. 1	159. 2	153. 7	224. 2	236. 0	272. 8	287. 1
300	337. 8	152. 6	165. 0	159. 3	232. 0	244. 2	282. 2	297. 0
310	349. 0	158. 0	170. 7	164. 9	239. 7	252. 3	291. 6	306. 9
320	360. 3	163. 5	176. 5	170. 5	247. 5	260. 5	301. 0	316. 8
330	371. 5	168. 9	182. 3	176. 1	255. 3	268. 7	310. 4	326. 7
340	382. 8	174. 5	188. 1	181. 8	263. 0	276. 8	319. 8	336. 6
350	394. 0	180. 0	193. 9	187. 4	270. 7	285. 0	329. 2	346. 5
360	405. 3	185. 5	199. 7	193. 1	278. 4	293. 1	338. 6	356. 4
370	416. 6	191. 1	205. 5	198. 8	286. 2	301. 3	348. 0	366. 3
380	427. 8	196. 7	211. 4	204. 5	293. 9	309. 4	357. 4	376. 2
390	439. 1	202. 3	217. 3	210. 2	301. 6	317. 5	366. 8	386. 1
400	450. 3	208. 0	223. 2	216. 0	309. 4	325. 7	376. 2	396. 0
410	461. 6	213. 7	229. 1	221. 8	317. 1	333. 8	385. 6	405. 9
420	472. 9	219. 4	235. 0	227. 6	324. 9	342. 0	395. 0	415. 8
430	484. 1	225. 1	240. 9	233. 4	332. 6	350. 1	404. 4	425. 7
440	495. 4	230. 8	246. 9	239. 2	340. 4	358. 3	413. 8	435. 6
450	506. 6	236. 6	252. 9	245. 0	348. 1	366. 4	423. 2	445. 5
460	517. 9	242. 4	258. 9	250. 9	355. 9	374. 6	432. 6	455. 4
470	529. 1	248. 1	264. 9	256. 8	363. 6	382. 7	442. 0	465. 3
480	540. 4	253. 8	270. 9	262. 7	371. 3	390. 9	451. 4	475. 2

TABLE 81.—*Bertrand table for reducing sugars*

A. DETERMINATION OF INVERT SUGAR, GLUCOSE, GALACTOSE, MALTOSE, AND LACTOSE

Milligrams of sugar	Weight of copper corresponding to—					Milligrams of of sugar	Weight of copper corresponding to—				
	Invert sugar	Glucose	Galactose	Maltose anhyd	Lactose anhyd		Invert sugar	Glucose	Galactose	Maltose anhyd	Lactose anhyd
	mg Cu	*mg* Cu	*mg* Cu	*mg* Cu	*mg* Cu		*mg* Cu	*mg* Cu	*mg* Cu	*mg* Cu	*mg* Cu
10	20.6	20.4	19.3	11.2	14.4	56	105.7	105.8	101.5	61.4	76.2
11	22.6	22.4	21.2	12.3	15.8	57	107.4	107.6	103.2	62.5	77.5
12	24.6	24.3	23.0	13.4	17.2	58	109.2	109.3	104.9	63.5	78.8
13	26.5	26.3	24.9	14.5	18.6	59	110.9	111.1	106.6	64.6	80.1
14	28.5	28.3	26.7	15.6	20.0	60	112.6	112.8	108.3	65.7	81.4
15	30.5	30.2	28.6	16.7	21.4	61	114.3	114.5	110.0	66.8	82.7
16	32.5	32.2	30.5	17.8	22.8	62	115.9	116.2	111.6	67.9	83.9
17	34.5	34.2	32.3	18.9	24.2	63	117.6	117.9	113.3	68.9	85.2
18	36.4	36.2	34.2	20.0	25.6	64	119.2	119.6	115.0	70.0	86.5
19	38.4	38.1	36.0	21.1	27.0	65	120.9	121.3	116.6	71.1	87.7
20	40.4	40.1	37.9	22.2	28.4	66	122.6	123.0	118.3	72.2	89.9
21	42.3	42.0	39.7	23.3	29.8	67	124.2	124.7	120.0	73.3	90.3
22	44.2	43.9	41.6	24.4	31.1	68	125.9	126.4	121.7	74.3	91.6
24	48.0	47.7	45.2	26.6	33.9	69	127.5	128.1	123.3	75.4	92.8
25	49.8	49.6	47.0	27.7	35.2	70	129.2	129.8	125.0	76.5	94.1
26	51.7	51.5	48.9	28.9	36.6	71	130.8	131.4	126.6	77.6	95.4
27	53.6	53.4	50.7	30.0	38.0	72	132.4	133.1	128.3	78.6	96.9
28	55.5	55.3	52.5	31.1	39.4	73	134.0	134.7	130.0	79.7	98.0
29	57.4	57.2	54.4	32.2	40.7	74	135.6	136.3	131.5	80.8	99.1
30	59.3	59.1	56.2	33.3	42.1	75	137.2	137.9	133.1	81.8	100.4
31	61.1	60.9	58.0	34.4	43.4	76	138.9	139.6	134.8	82.9	101.7
32	63.0	62.8	59.7	35.5	44.8	77	140.5	141.2	136.4	84.0	102.9
33	64.8	64.6	61.5	36.5	46.1	78	142.1	142.8	138.0	85.1	104.2
34	66.7	66.5	63.3	37.6	47.4	79	143.7	144.5	139.7	86.1	105.4
35	68.5	68.3	65.0	38.7	48.7	80	145.3	146.1	141.3	87.2	106.7
36	70.3	70.1	66.8	39.8	50.1	81	146.9	147.7	142.9	88.3	107.9
37	72.2	72.0	68.6	40.9	51.4	82	148.5	149.3	144.6	89.4	109.2
38	74.0	73.8	70.4	41.9	52.7	83	150.0	150.9	146.2	90.4	110.4
39	75.9	75.7	72.1	43.0	54.1	84	151.6	152.5	147.8	91.5	111.7
40	77.7	77.5	73.9	44.1	55.4	85	153.2	154.0	149.4	92.6	112.9
41	79.5	79.3	75.6	45.2	56.7	86	154.8	155.6	151.1	93.7	114.1
42	81.2	81.1	77.4	46.3	58.0	87	156.4	157.2	152.7	94.8	115.4
43	83.0	82.9	79.1	47.4	59.3	88	157.9	158.8	154.3	95.8	116.6
44	84.8	84.7	80.8	48.5	60.6	89	159.5	160.4	156.0	96.9	117.9
45	86.5	86.4	82.5	49.5	61.9	90	161.1	162.0	157.6	98.0	119.1
46	88.3	88.2	84.3	50.6	63.3	91	162.6	163.6	159.2	99.0	120.3
47	90.1	90.0	86.0	51.7	64.6	92	164.2	165.2	160.8	100.1	121.6
48	91.9	91.8	87.7	52.8	65.9	93	165.7	166.7	162.4	101.1	122.8
49	93.6	93.6	89.5	53.9	67.2	94	167.3	168.3	164.0	102.2	124.0
50	95.4	95.4	91.2	55.0	68.5	95	168.8	169.9	165.6	103.2	125.2
51	97.1	97.1	92.9	56.1	69.8	96	170.3	171.5	167.2	104.2	126.5
52	98.8	98.9	94.6	57.1	71.1	97	171.9	173.1	168.8	105.3	127.7
53	100.6	100.6	96.3	58.2	72.4	98	173.4	174.6	170.4	106.3	128.9
54	102.2	102.3	98.0	59.3	73.7	99	175.0	176.2	172.0	107.4	130.2
55	104.0	104.1	99.7	60.3	74.9	100	176.5	177.8	173.6	108.4	131.4

B. DETERMINATION OF MANNOSE, ARABINOSE, SORBOSE, AND XYLOSE

Milligrams of sugar	Weight of copper corresponding to—				Milligrams of sugar	Weight of copper corresponding to—			
	Mannose	Arabinose	Sorbose	Xylose		Mannose	Arabinose	Sorbose	Xylose
	mg Cu	*mg* Cu	*mg* Cu	*mg* Cu		*mg* Cu	*mg* Cu	*mg* Cu	*mg* Cu
10	20.7	21.2	15.4	20.1	60	113.3	119.3	88.4	113.2
20	40.5	41.9	30.5	39.6	70	130.2	137.5	102.3	130.6
30	59.5	62.0	45.3	58.7	80	146.9	155.3	115.9	147.6
40	78.0	81.5	59.9	77.3	90	163.3	172.7	129.4	164.2
50	95.9	100.6	74.2	95.4	100	179.4	189.8	142.8	180.5

TABLE 82.—*Herzfeld table for determining invert sugar in raw sugars (invert sugar not to exceed 1.5 percent)*

Copper	Invert sugar	Copper	Invert sugar	Copper	Invert sugar	Copper	Invert sugar	Copper	Invert sugar
mg	%	*mg*	%	*mg*	%	*mg*	%	*mg*	%
50	0.050	105	0.325	160	0.621	215	0.929	270	1.242
51	.054	106	.330	161	.627	216	.935	271	1.248
52	.058	107	.335	162	.633	217	.940	272	1.253
53	.062	108	.340	163	.639	218	.946	273	1.259
54	.066	109	.346	164	.645	219	.951	274	1.265
55	.070	110	.351	165	.651	220	.957	275	1.271
56	.074	111	.356	166	.657	221	.962	276	1.276
57	.078	112	.361	167	.663	222	.968	277	1.282
58	.082	113	.366	168	.669	223	.973	278	1.288
59	.086	114	.371	169	.675	224	.979	279	1.294
60	.090	115	.376	170	.680	225	.984	280	1.299
61	.094	116	.381	171	.686	226	.990	281	1.305
62	.098	117	.386	172	.692	227	.996	282	1.311
63	.103	118	.392	173	.698	228	1.001	283	1.317
64	.108	119	.397	174	.704	229	1.007	284	1.322
65	.113	120	.402	175	.709	230	1.013	285	1.328
66	.118	121	.407	176	.715	231	1.018	286	1.334
67	.123	122	.412	177	.720	232	1.024	287	1.339
68	.128	123	.417	178	.726	233	1.030	288	1.345
69	.133	124	.423	179	.731	234	1.036	289	1.351
70	.138	125	.428	180	.737	235	1.041	290	1.357
71	.143	126	.433	181	.742	236	1.047	291	1.362
72	.148	127	.438	182	.748	237	1.053	292	1.368
73	.152	128	.443	183	.753	238	1.058	293	1.374
74	.157	129	.448	184	.759	239	1.064	294	1.380
75	.162	130	.453	185	.764	240	1.070	295	1.385
76	.167	131	.458	186	.770	241	1.076	296	1.391
77	.172	132	.463	187	.775	242	1.081	297	1.397
78	.177	133	.468	188	.781	243	1.087	298	1.403
79	.182	134	.473	189	.786	244	1.093	299	1.408
80	.187	135	.478	190	.792	245	1.099	300	1.414
81	.192	136	.483	191	.797	246	1.104	301	1.420
82	.197	137	.488	192	.803	247	1.110	302	1.425
83	.202	138	.493	193	.808	248	1.116	303	1.431
84	.208	139	.498	194	.814	249	1.122	304	1.437
85	.213	140	.503	195	.819	250	1.127	305	1.443
86	.219	141	.509	196	.825	251	1.133	306	1.448
87	.225	142	.515	197	.830	252	1.139	307	1.454
88	.231	143	.521	198	.836	253	1.144	308	1.460
89	.236	144	.527	199	.841	254	1.150	309	1.466
90	.242	145	.533	200	.847	255	1.156	310	1.471
91	.248	146	.538	201	.852	256	1.162	311	1.477
92	.254	147	.544	202	.858	257	1.167	312	1.483
93	.260	148	.550	203	.863	258	1.173	313	1.489
94	.265	149	.556	204	.869	259	1.179	314	1.494
								315	1.500
95	.271	150	.562	205	.874	260	1.185		
96	.277	151	.568	206	.880	261	1.190		
97	.283	152	.574	207	.885	262	1.196		
98	.288	153	.580	208	.891	263	1.202		
99	.294	154	.586	209	.896	264	1.207		
100	.300	155	.592	210	.902	265	1.213		
101	.305	156	.598	211	.907	266	1.219		
102	.310	157	.604	212	.913	267	1.225		
103	.315	158	.609	213	.918	268	1.231		
104	.320	159	.615	214	.924	269	1.236		

TABLE 83.—*Determination of invert sugar by Vondrak's modification of the Herzfeld method*

[Add five roughened glass beads]

Copper	Sucrose (grams)			Copper	Sucrose (grams)		
	10	2.5	0		10	2.5	0
	Invert sugar				Invert sugar		
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
5	----------	----------	2	80	28	35	43
10	----------	----------	5	85	30	38	45
15	----------	----------	8	90	33	41	48
20	----------	3	10	95	35	43	51
25	----------	6	13	100	38	46	54
30	----------	9	15	110	43	52	59
35	3	11	18	120	48	58	65
40	6	13	21	130	53	64	70
45	9	16	24	140	59	70	76
50	12	19	27	150	65	77	81
55	14	22	29	160	71	83	87
60	17	25	32	170	78	89	92
65	20	27	35	180	84	95	98
70	23	30	37	190	90	----------	----------
75	25	33	40	200	96	----------	----------

TABLE 84.—*Meissl and Hiller factors for invert sugar*[1]

[Where more than 1.5% is invert sugar and less than 98.5% is sucrose]

Ratio of sucrose to invert sugar=*R:I*	Approximate absolute weight of invert sugar (Z)						
	200 mg	175 mg	150 mg	125 mg	100 mg	75 mg	50 mg
0:100	56.4	55.4	54.5	53.8	53.2	53.0	53.0
10:90	56.3	55.3	54.4	53.8	53.2	52.9	52.9
20:80	56.2	55.2	54.3	53.7	53.2	52.7	52.7
30:70	56.1	55.1	54.2	53.7	53.2	52.6	52.6
40:60	55.9	55.0	54.1	53.6	53.1	52.5	52.4
50:50	55.7	54.9	54.0	53.5	53.1	52.3	52.2
60:40	55.6	54.7	53.8	53.2	52.8	52.1	51.9
70:30	55.5	54.5	53.5	52.9	52.5	51.9	51.6
80:20	55.4	54.3	53.3	52.7	52.2	51.7	51.3
90:10	54.6	53.6	53.1	52.6	52.1	51.6	51.2
91:9	54.1	53.6	52.6	52.1	51.6	51.2	50.7
92:8	53.6	53.1	52.1	51.6	51.2	50.7	50.3
93:7	53.6	53.1	52.1	51.2	50.7	50.3	49.8
94:6	53.1	52.6	51.6	50.7	50.3	49.8	48.9
95:5	52.6	52.1	51.2	50.3	49.4	48.9	48.5
96:4	52.1	51.2	50.7	49.8	48.9	47.7	46.9
97:3	50.7	50.3	49.8	48.9	47.7	46.2	45.1
98:2	49.9	48.9	48.5	47.3	45.8	43.3	40.0
99:1	47.7	47.3	46.5	45.1	43.3	41.2	38.1

[1] Z. Ver. Rübenzucker-Ind. **39** [N. F. 26] 734 (1889).

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TABLE 85.—*Factors for 10 ml of Soxhlet solution to be used in connection with the Lane and Eynon general volumetric method*

Titer	Invert sugar (sucrose absent)	1 g of sucrose per 100 ml of invert sugar	5 g of sucrose per 100 ml of invert sugar	10 g of sucrose per 100 ml of invert sugar	25 g of sucrose per 100 ml of invert sugar	Dextrose	Levulose	Anhydrous maltose, $C_{12}H_{22}O_{11}$	Hydrated maltose, $C_{12}H_{22}O_{11}$, H_2O	Anhydrous lactose, $C_{12}H_{22}O_{11}$	Hydrated lactose, $C_{12}H_{22}O_{11}.H_2O$
ml											
15	50. 5	49. 9	47. 6	46. 1	43. 4	49. 1	52. 2	77. 2	81. 3	64. 9	68. 3
16	50. 6	50. 0	47. 6	46. 1	43. 4	49. 2	52. 3	77. 1	81. 2	64. 8	68. 2
17	50. 7	50. 1	47. 6	46. 1	43. 4	49. 3	52. 3	77. 0	81. 1	64. 8	68. 2
18	50. 8	50. 1	47. 6	46. 1	43. 3	49. 3	52. 4	77. 0	81. 0	64. 7	68. 1
19	50. 8	50. 2	47. 6	46. 1	43. 3	49. 4	52. 5	76. 9	80. 9	64. 7	68. 1
20	50. 9	50. 2	47. 6	46. 1	43. 2	49. 5	52. 5	76. 8	80. 8	64. 6	68. 0
21	51. 0	50. 2	47. 6	46. 1	43. 2	49. 5	52. 6	76. 7	80. 7	64. 6	68. 0
22	51. 0	50. 3	47. 6	46. 1	43. 1	49. 6	52. 7	76. 6	80. 6	64. 6	68. 0
23	51. 1	50. 3	47. 6	46. 1	43. 0	49. 7	52. 7	76. 5	80. 5	64. 5	67. 9
24	51. 2	50. 3	47. 6	46. 1	42. 9	49. 8	52. 8	76. 4	80. 4	64. 5	67. 9
25	51. 2	50. 4	47. 6	46. 0	42. 8	49. 8	52. 8	76. 4	80. 4	64. 5	67. 9
26	51. 3	50. 4	47. 6	46. 0	42. 8	49. 9	52. 9	76. 3	80. 3	64. 5	67. 9
27	51. 4	50. 4	47. 6	46. 0	42. 7	49. 9	52. 9	76. 2	80. 2	64. 4	67. 8
28	51. 4	50. 5	47. 7	46. 0	42. 7	50. 0	53. 0	76. 1	80. 1	64. 4	67. 8
29	51. 5	50. 5	47. 7	46. 0	42. 6	50. 0	53. 1	76. 0	80. 0	64. 4	67. 8
30	51. 5	50. 5	47. 7	46. 0	42. 5	50. 1	53. 2	76. 0	80. 0	64. 4	67. 8
31	51. 6	50. 6	47. 7	45. 9	42. 5	50. 2	53. 2	75. 9	79. 9	64. 4	67. 8
32	51. 6	50. 6	47. 7	45. 9	42. 4	50. 2	53. 3	75. 9	79. 9	64. 4	67. 8
33	51. 7	50. 6	47. 7	45. 9	42. 3	50. 3	53. 3	75. 8	79. 8	64. 4	67. 8
34	51. 7	50. 6	47. 7	45. 8	42. 2	50. 3	53. 4	75. 8	79. 8	64. 4	67. 9
35	51. 8	50. 7	47. 7	45. 8	42. 2	50. 4	53. 4	75. 7	79. 7	64. 5	67. 9
36	51. 8	50. 7	47. 7	45. 8	42. 1	50. 4	53. 5	75. 6	79. 6	64. 5	67. 9
37	51. 9	50. 7	47. 7	45. 7	42. 0	50. 5	53. 5	75. 6	79. 6	64. 5	67. 9
38	51. 9	50. 7	47. 7	45. 7	42. 0	50. 5	53. 6	75. 5	79. 5	64. 5	67. 9
39	52. 0	50. 8	47. 7	45. 7	41. 9	50. 6	53. 6	75. 5	79. 5	64. 5	67. 9
40	52. 0	50. 8	47. 7	45. 6	41. 8	50. 6	53. 6	75. 4	79. 4	64. 5	67. 9
41	52. 1	50. 8	47. 7	45. 6	41. 8	50. 7	53. 7	75. 4	79. 4	64. 6	68. 0
42	52. 1	50. 8	47. 7	45. 6	41. 7	50. 7	53. 7	75. 3	79. 3	64. 6	68. 0
43	52. 2	50. 8	47. 7	45. 5	41. 6	50. 8	53. 8	75. 3	79. 3	64. 6	68. 0
44	52. 2	50. 9	47. 7	45. 5	41. 5	50. 8	53. 8	75. 2	79. 2	64. 6	68. 0
45	52. 3	50. 9	47. 7	45. 4	41. 4	50. 9	53. 9	75. 2	79. 2	64. 7	68. 1
46	52. 3	50. 9	47. 7	45. 4	41. 4	50. 9	53. 9	75. 1	79. 1	64. 7	68. 1
47	52. 4	50. 9	47. 7	45. 3	41. 3	51. 0	53. 9	75. 1	79. 1	64. 8	68. 2
48	52. 4	50. 9	47. 7	45. 3	41. 2	51. 0	54. 0	75. 1	79. 1	64. 8	68. 2
49	52. 5	51. 0	47. 7	45. 2	41. 1	51. 0	54. 0	75. 0	79. 0	64. 8	68. 2
50	52. 5	51. 0	47. 7	45. 2	41. 0	51. 1	54. 0	75. 0	79. 0	64. 9	68. 3

TABLE 86.—*Factors for 25 ml of Soxhlet solution to be used in connection with the Lane and Eynon general volumetric method*

Titer	Invert sugar (sucrose absent)	1 g of sucrose per 100 ml of invert sugar	Dextrose	Levulose	Anhydrous maltose, $C_{12}H_{22}O_{11}$	Hydrated maltose, $C_{12}H_{22}O_{11}.H_2O$	Anhydrous lactose, $C_{12}H_{22}O_{11}$	Hydrated lactose, $C_{12}H_{22}O_{11}.H_2O$
ml								
15	123. 6	122. 6	120. 2	127. 4	197. 8	208. 2	163. 9	172. 5
16	123. 6	122. 7	120. 2	127. 4	197. 4	207. 8	163. 5	172. 1
17	123. 6	122. 7	120. 2	127. 5	197. 0	207. 4	163. 1	171. 7
18	123. 7	122. 7	120. 2	127. 5	196. 7	207. 1	162. 8	171. 4
19	123. 7	122. 8	120. 3	127. 6	196. 5	206. 8	262. 5	171. 1
20	123. 8	122. 8	120. 3	127. 6	196. 2	206. 5	162. 3	170. 9
21	123. 8	122. 8	120. 3	127. 7	195. 8	206. 1	162. 0	170. 6
22	123. 9	122. 9	120. 4	127. 7	195. 5	205. 8	161. 8	170. 4
23	123. 9	122. 9	120. 4	127. 8	195. 1	205. 4	161. 6	170. 2
24	124. 0	122. 9	120. 5	127. 8	194. 8	205. 1	161. 5	170. 0
25	124. 0	123. 0	120. 5	127. 9	194. 5	204. 8	161. 4	169. 9
26	124. 1	123. 0	120. 6	127. 9	194. 2	204. 4	161. 2	169. 7
27	124. 1	123. 0	120. 6	128. 0	193. 9	204. 1	161. 0	169. 5
28	124. 2	123. 1	120. 7	128. 0	193. 6	203. 8	160. 8	169. 3
29	124. 2	123. 1	120. 7	128. 1	193. 3	203. 5	160. 7	169. 2
30	124. 3	123. 1	120. 8	128. 1	193. 0	203. 2	160. 6	169. 0
31	124. 3	123. 2	120. 8	128. 1	192. 8	202. 9	160. 5	168. 9
32	124. 4	123. 2	120. 8	128. 2	192. 5	202. 6	160. 4	168. 8
33	124. 4	123. 2	120. 9	128. 2	192. 2	202. 3	160. 2	168. 6
34	124. 5	123. 3	120. 9	128. 3	191. 9	202. 0	160. 1	168. 5
35	124. 5	123. 3	121. 0	128. 3	191. 7	201. 8	160. 0	168. 4
36	124. 6	123. 3	121. 0	128. 4	191. 4	201. 5	159. 8	168. 2
37	124. 6	123. 4	121. 1	128. 4	191. 2	201. 2	159. 7	168. 1
38	124. 7	123. 4	121. 2	128. 5	191. 0	201. 0	159. 6	168. 0
39	124. 7	123. 4	121. 2	128. 5	190. 8	200. 8	169. 5	167. 9
40	124. 8	123. 4	121. 2	128. 6	190. 5	200. 5	159. 4	167. 8
41	124. 8	123. 5	121. 3	128. 6	190. 3	200. 3	159. 3	167. 7
42	124. 9	123. 5	121. 4	128. 6	190. 1	200. 1	159. 2	167. 6
43	124. 9	123. 5	121. 4	128. 7	189. 8	199. 8	159. 2	167. 6
44	125. 0	123. 6	121. 5	128. 7	189. 6	199. 6	159. 1	167. 5
45	125. 0	123. 6	121. 5	128. 8	189. 4	199. 4	159. 0	167. 4
46	125. 1	123. 6	121. 6	128. 8	189. 2	199. 2	159. 0	167. 4
47	125. 1	123. 7	121. 6	128. 9	189. 0	199. 0	158. 9	167. 3
48	125. 2	123. 7	121. 7	128. 9	188. 9	198 9	158. 8	167. 2
49	125. 2	123. 7	121. 7	129. 0	188. 8	198. 7	158. 8	167. 2
50	125. 3	123. 8	121. 8	129. 0	188. 7	198. 6	158. 7	167. 1

TABLE 87.—*Burette readings for solutions containing 25 g of sugar sample plus 0.1 g of added invert sugar per 100 ml*

[10 ml of Fehling solution used]

Solution required	Invert sugar in sugar sample	Solution required	Invert sugar in sugar sample
ml	*Percent*	*ml*	*Percent*
20	0.464	32	0.128
21	.423	33	.111
22	.384	34	.095
23	.348	35	.080
24	.315	36	.066
25	.284	37	.052
26	.257	38	.040
27	.232	39	.028
28	.209	40	.017
29	.188	41	.008
30	.168	41.7	.000
31	.148	--------	----------

TABLE 88.—*Corrections, in milliliters, to be added to burette readings in the titration of lactose solutions containing three or six times as much sucrose as lactose*

Sugar solution required	10 ml of Fehling solution		25 ml of Fehling solution	
	Ratio of sucrose to lactose		Ratio of sucrose to lactose	
	3:1	6:1	3:1	6:1
ml	*ml*	*ml*	*ml*	*ml*
15	0.15	0.30	0.30	0.60
20	.25	.50	.30	.60
25	.30	.60	.35	.65
30	.35	.70	.35	.70
35	.40	.80	.40	.80
40	.45	.90	.45	.90
45	.50	.95	.55	1.10
50	.55	1.05	.60	1.20

TABLE 89.—*Factors for the Lane and Eynon volumetric method for mixtures of dextrose and levulose*

The factor represents the number of miligrams of sugar required to reduce 25 ml of Soxhlet reagent.

$$100 \times \frac{\text{factor}}{\text{titer}} = \text{mg of sugar in 100 ml.}$$

Titer	Dextrose	90 D 10 L	80 D 20 L	70 D 30 L	60 D 40 L	50 D 50 L	40 D 60 L
ml							
15	120. 2	120. 9	121. 6	122. 2	122. 9	123. 6	124. 4
16	120. 2	120. 9	121. 6	122. 2	122. 9	123. 6	124. 4
17	120. 2	120. 9	121. 6	122. 2	122. 9	123. 6	124. 4
18	120. 2	120. 9	121. 6	122. 3	123. 0	123. 7	124. 5
19	120. 3	121. 0	121. 7	122. 3	123. 0	123. 7	124. 5
20	120. 3	121. 0	121. 7	122. 4	123. 1	123. 8	124. 6
21	120. 3	121. 0	121. 7	122. 4	123. 1	123. 8	124. 6
22	120. 4	121. 1	121. 8	122. 5	123. 2	123. 9	124. 7
23	120. 4	121. 1	121. 8	122. 5	123. 2	123. 9	124. 7
24	120. 5	121. 2	121. 9	122. 6	123. 3	124. 0	124. 8
25	120. 5	121. 2	121. 9	122. 6	123. 3	124. 0	124. 8
26	120. 6	121. 3	122. 0	122. 7	123. 4	124. 1	124. 9
27	120. 6	121. 3	122. 0	122. 7	123. 4	124. 1	124. 9
28	120. 7	121. 4	122. 1	122. 8	123. 5	124. 2	125. 0
29	120. 7	121. 4	122. 1	122. 8	123. 5	124. 2	125. 0
30	120. 8	121. 5	122. 2	122. 9	123. 6	124. 3	125. 1
31	120. 8	121. 5	122. 2	122. 9	123. 6	124. 3	125. 1
32	120. 8	121. 5	122. 2	123. 0	123. 7	124. 4	125. 2
33	120. 9	121. 6	122. 3	123. 0	123. 7	124. 4	125. 2
34	120. 9	121. 6	122. 3	123. 1	123. 8	124. 5	125. 3
35	121. 0	121. 7	122. 4	123. 1	123. 8	124. 5	125. 3
36	121. 0	121. 7	122. 4	123. 2	123. 9	124. 6	125. 4
37	121. 1	121. 8	122. 5	123. 2	123. 9	124. 6	125. 4
38	121. 2	121. 9	122. 6	123. 3	124. 0	124. 7	125. 5
39	121. 2	121. 9	122. 6	123. 3	124. 0	124. 7	125. 5
40	121. 2	121. 9	122. 6	123. 4	124. 1	124. 8	125. 6
41	121. 3	122. 0	122. 7	123. 4	124. 1	124. 8	125. 6
42	121. 4	122. 1	122. 8	123. 5	124. 2	124. 9	125. 6
43	121. 4	122. 1	122. 8	123. 5	124. 2	124. 9	125. 7
44	121. 5	122. 2	122. 9	123. 6	124. 3	125. 0	125. 7
45	121. 5	122. 2	122. 9	123. 6	124. 3	125. 0	125. 8
46	121. 6	122. 3	123. 0	123. 7	124. 4	125. 1	125. 8
47	121. 6	122. 3	123. 0	123. 7	124. 4	125. 1	125. 9
48	121. 7	122. 4	123. 1	123. 8	124. 5	125. 2	125. 9
49	121. 7	122. 4	123. 1	123. 8	124. 5	125. 2	126. 0
50	121. 8	122. 5	123. 2	123. 9	124. 6	125. 3	126. 0

TABLE 89.—*Factors for the Lane and Eynon volumetric method for mixtures of dextrose and levulose*—Continued

In the last three columns are titer corrections corresponding to experimentally determined factors which differ from the tabulated factors by 1, 2, and 3 units. When the experimental factor is greater than the tabulated, the correction is to be subtracted from the observed titer, and vice versa. This corrected titer is to be used with the tabulated factor.

Titer	30 D 70 L	20 D 80 L	10 D 90 L	Levulose	Titer corrections		
					1	2	3
ml					*ml*	*ml*	*ml*
15	125. 1	125. 9	126. 6	127. 4	0. 12	0. 24	0. 37
16	125. 1	125. 9	126. 6	127. 4	. 13	. 26	. 39
17	125. 2	125. 9	126. 7	127. 5	. 14	. 28	. 41
18	125. 2	126. 0	126. 7	127. 5	. 15	. 30	. 44
19	125. 3	126. 0	126. 8	127. 6	. 15	. 31	. 46
20	125. 3	126. 1	126. 8	127. 6	. 16	. 33	. 49
21	125. 4	126. 1	126. 9	127. 7	. 17	. 34	. 51
22	125. 4	126. 2	126. 9	127. 7	. 18	. 36	. 54
23	125. 5	126. 2	127. 0	127. 8	. 19	. 37	. 56
24	125. 5	126. 3	127. 0	127. 8	. 20	. 39	. 59
25	125. 6	126. 3	127. 1	127. 9	. 20	. 41	. 61
26	125. 6	126. 4	127. 1	127. 9	. 21	. 42	. 63
27	125. 7	126. 4	127. 2	128. 0	. 22	. 44	. 66
28	125. 7	126. 5	127. 2	128. 0	. 23	. 45	. 68
29	125. 8	126. 5	127. 3	128. 1	. 24	. 47	. 71
30	125. 8	126. 6	127. 3	128. 1	. 25	. 49	. 73
31	125. 8	126. 6	127. 3	128. 1	. 25	. 50	. 76
32	125. 9	126. 7	127. 4	128. 2	. 26	. 52	. 78
33	125. 9	126. 7	127. 4	128. 2	. 27	. 54	. 80
34	126. 0	126. 8	127. 5	128. 3	. 28	. 55	. 83
35	126. 0	126. 8	127. 5	128. 3	. 29	. 57	. 85
36	126. 1	126. 9	127. 6	128. 4	. 29	. 59	. 88
37	126. 1	126. 9	127. 6	128. 4	. 30	. 60	. 90
38	126. 2	127. 0	127. 7	128. 5	. 31	. 62	. 93
39	126. 2	127. 0	127. 7	128. 5	. 32	. 63	. 95
40	126. 3	127. 1	127. 8	128. 6	. 33	. 65	. 98
41	126. 3	127. 1	127. 8	128. 6	. 33	. 67	1. 00
42	126. 4	127. 1	127. 9	128. 6	. 34	. 68	1. 02
43	126. 4	127. 2	127. 9	128. 7	. 35	. 70	1. 05
44	126. 5	127. 2	128. 0	128. 7	. 36	. 72	1. 07
45	126. 5	127. 3	128. 0	128. 8	. 37	. 73	1. 10
46	126. 6	127. 3	128. 1	128. 8	. 37	. 75	1. 12
47	126. 6	127. 4	128. 1	128. 9	. 38	. 76	1. 15
48	126. 7	127. 4	128. 2	128. 9	. 39	. 78	1. 17
49	126. 7	127. 5	128. 2	129. 0	. 40	. 80	1. 20
50	126. 8	127. 5	128. 3	129. 0	. 41	. 81	1. 22

TABLE 90.—*Zerban and Wiley factors for mixtures of dextrose and levulose (Lane and Eynon method)*

[10 ml of Soxhlet solution]

Titer	100 D 0 L	90 D 10 L	80 D 20 L	70 D 30 L	60 D 40 L	50 D 50 L	40 D 60 L	30 D 70 L	20 D 80 L	10 D 90 L	0 D 100 L
IN THE PRESENCE OF 10 G OF SUCROSE IN 100 ML											
15	46. 1	46. 3	46. 5	46. 6	46. 8	47. 0	47. 2	47. 4	47. 7	47. 9	48. 1
20	45. 8	46. 0	46. 2	46. 3	46. 5	46. 7	46. 9	47. 1	47. 3	47. 5	47. 7
25	45. 5	45. 7	45. 8	45. 9	46. 1	46. 3	46. 5	46. 7	46. 9	47. 1	47. 3
30	45. 2	45. 4	45. 5	45. 7	45. 8	46. 0	46. 2	46. 4	46. 5	46. 7	46. 9
35	45. 0	45. 1	45. 3	45. 4	45. 6	45. 7	45. 9	46. 1	46. 2	46. 4	46. 6
40	44. 9	45. 0	45. 2	45. 3	45. 5	45. 6	45. 8	45. 9	46. 1	46. 3	46. 4
45	44. 8	44. 9	45. 1	45. 2	45. 4	45. 5	45. 6	45. 8	45. 9	46. 1	46. 2
50	44. 7	44. 8	45. 0	45. 1	45. 3	45. 4	45. 5	45. 7	45. 8	46. 0	46. 1
IN THE PRESENCE OF 25 G OF SUCROSE IN 100 ML											
15	42. 9	43. 1	43. 2	43. 4	43. 6	43. 7	43. 9	44. 1	44. 3	44. 5	44. 7
20	42. 6	42. 7	42. 9	43. 0	43. 1	43. 2	43. 4	43. 5	43. 7	43. 8	44. 0
25	42. 3	42. 4	42. 5	42. 6	42. 7	42. 8	42. 9	43. 1	43. 2	43. 4	43. 5
30	42. 0	42. 1	42. 2	42. 3	42. 4	42. 5	42. 6	42. 7	42. 8	42. 9	43. 0
35	41. 6	41. 7	41. 8	41. 9	42. 0	42. 1	42. 2	42. 3	42. 4	42. 5	42. 6
40	41. 3	41. 4	41. 5	41. 6	41. 7	41. 8	41. 9	42. 0	42. 1	42. 2	42. 3
45	40. 9	41. 0	41. 1	41. 2	41. 3	41. 4	41. 5	41. 6	41. 7	41. 8	41. 9
50	40. 5	40. 6	40. 7	40. 8	40. 9	41. 0	41. 1	41. 2	41. 3	41. 4	41. 5

TABLE 91.—*Lane and Eynon factors and reducing ratios for determinination of dextrose and levulose in raw sugars*

[10-ml of Soxhlet solution]

10 grams of sucrose				25 grams of sucrose			
Titer	Lane and Eynon factor	Reducing ratio, *a*	$a-0.0806$	Titer	Lane and Eynon factor	Reducing ratio, *a*	$a-0.0806$
ml				*ml*			
15	48. 1	1. 0434	0. 9628	15	44. 7	1. 0419	0. 9613
20	47. 7	1. 0414	. 9608	20	44. 0	1. 0324	. 9518
25	47. 3	1. 0394	. 9588	25	43. 5	1. 0273	. 9467
30	46. 9	1. 0374	. 9568	30	43. 0	1. 0248	. 9442
35	46. 6	1, 0354	. 9548	35	42. 6	1. 0246	. 9440
40	46. 4	1, 0334	. 9528	40	42. 3	1. 0245	. 9439
45	46. 2	1. 0314	. 9508	45	41. 9	1. 0244	. 9438
50	46. 1	1. 0311	. 9505	50	41. 5	1. 0234	. 9437

TABLE 92.—*Milligrams of dextrose and levulose corresponding to milligrams of cupric oxide or copper, and reduction ratio, a, according to Erb and Zerban, for various proportions of dextrose and levulose in the presence of sucrose (0.4 g of total sugar in 50 ml of solution), using the Munson and Walker method*

Cupric oxide	Copper	Levulose	Dextrose	Reduction ratio, *a*, for varying proportions between D and L									
				100 D 0 L	90 D 10 L	80 D 20 L	70 D 30 L	60 D 40 L	50 D 50 L	40 D 60 L	30 D 70 L	20 D 80 L	10 D 90 L
mg	*mg*	*mg*	*mg*										
50	39.9	18.3	16.3	1.119	1.121	1.123	1.125	1.127	1.129	1.127	1.126	1.125	1.124
75	59.9	29.2	26.2	1.115	1.118	1.120	1.123	1.125	1.127	1.126	1.125	1.125	1.124
100	79.9	40.2	36.2	1.111	1.114	1.117	1.120	1.123	1.125	1.125	1.125	1.125	1.124
125	99.9	51.3	46.3	1.108	1.111	1.114	1.117	1.120	1.123	1.123	1.123	1.124	1.124
150	119.8	62.5	56.6	1.105	1.108	1.111	1.114	1.117	1.119	1.120	1.121	1.122	1.124
175	139.8	73.8	67.0	1.101	1.104	1.107	1.110	1.112	1.114	1.116	1.117	1.118	1.119
200	159.8	85.1	77.5	1.098	1.101	1.103	1.106	1.108	1.110	1.111	1.112	1.113	1.114
225	179.8	96.5	88.0	1.096	1.097	1.099	1.101	1.103	1.105	1.106	1.107	1.108	1.108
250	199.7	108.0	98.8	1.093	1.095	1.097	1.098	1.099	1.100	1.101	1.102	1.103	1.103
275	219.7	119.6	109.8	1.089	1.091	1.093	1.093	1.095	1.095	1.096	1.096	1.097	1.096
300	239.7	131.2	120.8	1.086	1.087	1.088	1.089	1.090	1.091	1.091	1.090	1.090	1.090
325	259.6	142.9	131.8	1.084	1.085	1.086	1.086	1.086	1.086	1.086	1.086	1.085	1.085
350	279.6	154.8	143.2	1.081	1.081	1.082	1.082	1.082	1.082	1.082	1.082	1.081	1.081
375	299.6	166.7	154.5	1.079	1.079	1.078	1.078	1.077	1.077	1.077	1.077	1.077	1.077
400	319.6	178.6	165.8	1.077	1.077	1.076	1.075	1.074	1.073	1.073	1.073	1.072	1.072
425	339.5	190.6	177.5	1.074	1.073	1.071	1.070	1.069	1.068	1.068	1.068	1.068	1.068
450	359.5	202.8	189.2	1.072	1.070	1.069	1.067	1.065	1.064	1.064	1.064	1.063	1.063
475	379.5	215.0	200.9	1.070	1.067	1.065	1.063	1.061	1.059	1.059	1.058	1.057	1.057
500	399.5	227.1	212.8	1.067	1.064	1.061	1.059	1.057	1.055	1.054	1.053	1.052	1.052
525	419.4	239.4	224.8	1.065	1.062	1.059	1.056	1.053	1.050	1.050	1.050	1.049	1.049
550	439.4	251.9	237.1	1.062	1.059	1.055	1.032	1.049	1.046	1.046	1.046	1.046	1.046

TABLE 93.—*Copper-levulose equivalents according to the Jackson and Mathews modification of the Nyns selective method for levulose*

Cu	Levulose	Cu	Levulose	Cu	Levulose	Cu	Levulose	Cu	Levulose
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
1	0.6	20	7.9	39	13.7	58	19.1	77	24.5
2	1.1	21	8.2	40	13.9	59	19.4	78	24.8
3	1.6	22	8.5	41	14.2	60	19.7	79	25.1
4	2.1	23	8.9	42	14.5	61	20.0	80	25.4
5	2.5	24	9.2	43	14.8	62	20.3	81	25.7
6	2.9	25	9.5	44	15.1	63	20.6	82	25.9
7	3.3	26	9.8	45	15.4	64	20.9	83	26.2
8	3.7	27	10.1	46	15.7	65	21.2	84	26.5
9	4.1	28	10.4	47	16.0	66	21.4	85	26.8
10	4.5	29	10.7	48	16.3	67	21.7	86	27.0
11	4.8	30	11.0	49	16.6	68	22.0	87	27.3
12	5.1	31	11.3	50	16.8	69	22.2	88	27.6
13	5.5	32	11.6	51	17.1	70	22.5	89	27.9
14	5.9	33	11.9	52	17.4	71	22.8	90	28.1
15	6.2	34	12.2	53	17.7	72	23.1	91	28.4
16	6.5	35	12.5	54	18.0	73	23.4	92	28.7
17	6.9	36	12.8	55	18.3	74	23.7	93	29.0
18	7.2	37	13.1	56	18.6	75	24.0	94	29.2
19	7.6	38	13.4	57	18.9	76	24.2	95	29.5

TABLE 93.—*Copper-levulose equivalents according to the Jackson and Mathews modification of the Nyns selective method for levulose*—Continued

Cu	Levulose	Cu	Levulose	Cu	Levulose	Cu	Levulose	Cu	Levulose
mg	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
96	29. 8	140	42. 0	184	53. 6	228	65. 8	272	79. 7
97	30. 1	141	42. 3	185	53. 9	229	66. 1	273	80. 0
98	30. 4	142	42. 6	186	54. 2	230	66. 4	274	80. 4
99	30. 7	143	42. 8	187	54. 4	231	66. 7	275	80. 7
100	30. 9	144	43. 1	188	54. 7	232	67. 0	276	81. 0
101	31. 2	145	43. 4	189	54. 9	233	67. 3	277	81. 4
102	31. 5	146	43. 7	190	55. 2	234	67. 6	278	81. 7
103	31. 8	147	43. 9	191	55. 5	235	67. 9	279	82. 0
104	32. 1	148	44. 2	192	55. 7	236	68. 2	280	82. 4
105	32. 3	149	44. 5	193	56. 0	237	68. 5	281	82. 7
106	32. 6	150	44. 7	194	56. 3	238	68. 8	282	83. 1
107	32. 9	151	45. 0	195	56. 5	239	69. 1	283	83. 4
108	33. 2	152	45. 3	196	56. 8	240	69. 4	284	83. 8
109	33. 5	153	45. 6	197	57. 1	241	69. 7	285	84. 1
110	33. 7	154	45. 8	198	57. 3	242	70. 0	286	84. 4
111	34. 0	155	46. 1	199	57. 6	243	70. 3	287	84. 8
112	34. 3	156	46. 4	200	57. 9	244	70. 7	288	85. 1
113	34. 6	157	46. 6	201	58. 1	245	71. 0	289	85. 5
114	34. 8	158	46. 9	202	58. 4	246	71. 3	290	85. 9
115	35. 1	159	47. 1	203	58. 7	247	71. 6	291	86. 2
116	35. 4	160	47. 4	204	58. 9	248	71. 9	292	86. 6
117	35. 7	161	47. 7	205	59. 2	249	72. 2	293	86. 9
118	36. 0	162	47. 9	206	59. 4	250	72. 5	294	87. 3
119	26. 2	163	48. 2	207	59. 7	251	72. 8	295	87. 6
120	36. 5	164	48. 4	208	60. 0	252	73. 1	296	88. 0
121	36. 8	165	48. 7	209	60. 3	253	73. 5	297	88. 4
122	37. 1	166	49. 0	210	60. 6	254	73. 8	298	88. 7
123	37. 3	167	49. 2	211	60. 9	255	74. 1	299	89. 1
124	37. 6	168	49. 5	212	61. 1	256	74. 4	300	89. 5
125	37. 9	169	49. 7	213	61. 4	257	74. 7	301	89. 8
126	38. 2	170	50. 0	214	61. 7	258	75. 1	302	90. 2
127	38. 5	171	50. 2	215	62. 0	259	75. 4	303	90. 5
128	38. 7	172	50. 5	216	62. 3	260	75. 7	304	90. 9
129	39. 0	173	50. 8	217	62. 6	261	76. 0	305	91. 3
130	39. 3	174	51. 0	218	62. 9	262	76. 4	306	91. 7
131	39. 6	175	51. 3	219	63. 2	263	76. 7	307	92. 0
132	39. 9	176	51. 5	220	63. 4	264	77. 0	308	92. 4
133	40. 1	177	51. 8	221	63. 7	265	77. 4	309	92. 8
134	40. 4	178	52. 1	222	64. 0	266	77. 7	310	93. 2
135	40. 7	179	52. 3	223	64. 3	267	78. 1	311	93. 5
136	40. 9	180	52. 6	224	64. 6	268	78. 4	312	93. 9
137	41. 2	181	52. 8	225	64. 9	269	78. 7		
138	41. 5	182	53. 1	226	65. 2	270	79. 0		
139	41. 7	183	53. 4	227	65. 5	271	79. 4		

TABLE 94.—*Ratio of levulose to total sugar from the Lane and Eynon titration and Nyns "apparent" levulose*

Example illustrating the use of table 94.—Assume that a solution of levulose and dextrose gave a Lane and Eynon titer of 25.89 ml and that 20 ml of the same solution precipitated 247.3 mg of copper by the modified Nyns method. The original solution then contained by table 93 $(100 \times 71.7)/20 = 358.5$ mg of apparent levulose per 100 ml.

Then $$\frac{T \times l}{100} = \frac{25.89 \times 358.5}{100} = 92.8.$$

Referring to the values tabulated below we find opposite this product and under $T = 25$ the true ratio of levulose to total sugar to be 71.5 percent. The Lane and Eynon factor is 125.7, and the total sugar per 100 ml is $125.7/25.89 = 485.5$ mg, of which 71.5 percent (347.1 mg) is levulose and 138.4 mg is dextrose.

$\frac{T \times l}{100}$	$T=15$	$T=25$	$T=35$	$T=45$	$\frac{T \times l}{100}$	$T=15$	$T=25$	$T=35$	$T=45$
11	1. 2	1. 2	1. 1	1. 1	51	36. 5	36. 3	36. 1	35. 9
12	2. 1	2. 1	2. 0	2. 0	52	37. 3	37. 2	36. 9	36. 7
13	3. 0	3. 0	2. 9	2. 9	53	38. 2	38. 0	37. 8	37. 6
14	3. 9	3. 8	3. 8	3. 7	54	39. 1	38. 9	38. 6	38. 4
15	4. 8	4. 7	4. 7	4. 6	55	39. 9	39. 7	39. 5	39. 3
16	5. 7	5. 6	5. 6	5. 5	56	40. 8	40. 6	40. 3	40. 1
17	6. 5	6. 5	6. 4	6. 4	57	41. 7	41. 5	41. 2	40. 9
18	7. 4	7. 4	7. 3	7. 3	58	42. 5	42. 3	42. 1	41. 8
19	8. 3	8. 2	8. 2	8. 1	59	43. 4	43. 2	42. 9	42. 6
20	9. 2	9. 1	9. 1	9. 0	60	44. 2	44. 0	43. 8	43. 5
21	10. 1	10. 0	10. 0	9. 9	61	45. 0	44. 8	44. 6	44. 3
22	11. 0	10. 9	10. 9	10. 8	62	45. 9	45. 7	45. 5	45. 2
23	11. 9	11. 8	11. 8	11. 7	63	46. 7	46. 5	46. 3	46. 0
24	12. 8	12. 7	12. 6	12. 5	64	47. 6	47. 4	47. 2	46. 9
25	13. 7	13. 6	13. 5	13. 4	65	48. 4	48. 2	48. 0	47. 7
26	14. 5	14. 4	14. 3	14. 2	66	49. 3	49. 0	48. 8	48. 5
27	15. 4	15. 3	15. 2	15. 1	67	50. 1	49. 9	49. 7	49. 4
28	16. 3	16. 2	16. 1	16. 0	68	51. 0	50. 8	50. 6	50. 2
29	17. 2	17. 1	17. 0	16. 9	69	51. 8	51. 6	51. 4	51. 1
30	18. 1	18. 0	17. 9	17. 8	70	52. 7	52. 5	52. 2	51. 9
31	19. 0	18. 9	18. 7	18. 6	71	53. 5	53. 3	53. 1	52. 8
32	19. 9	19. 8	19. 6	19. 5	72	54. 3	54. 1	53. 9	53. 6
33	20. 8	20. 6	20. 5	20. 4	73	55. 2	55. 0	54. 7	54. 4
34	21. 6	21. 5	21. 4	21. 3	74	56. 0	55. 8	55. 6	55. 3
35	22. 5	22. 4	22. 3	22. 2	75	56. 8	56. 6	56. 4	56. 1
36	23. 4	23. 3	23. 2	23. 1	76	57. 7	57. 5	57. 2	56. 9
37	24. 3	24. 2	24. 0	23. 9	77	58. 5	58. 3	58. 1	57. 8
38	25. 2	25. 1	24. 9	24. 8	78	59. 4	59. 2	58. 9	58. 6
39	26. 1	26. 0	25. 8	25. 7	79	60. 2	60. 0	59. 8	59. 5
40	26. 9	26. 8	26. 6	26. 5	80	61. 1	60. 9	60. 6	60. 3
41	27. 8	27. 7	27. 5	27. 4	81	61. 9	61. 7	61. 4	61. 1
42	28. 7	28. 6	28. 4	28. 3	82	62. 8	62. 5	62. 3	62. 0
43	29. 5	29. 4	29. 2	29. 1	83	63. 6	63. 3	63. 1	62. 8
44	30. 4	30. 3	30. 1	30. 0	84	64. 4	64. 2	63. 9	63. 6
45	31. 3	31. 2	31. 0	30. 8	85	65. 2	65. 0	64. 8	64. 5
46	32. 2	32. 0	31. 9	31. 7	86	66. 0	65. 8	65. 6	65. 3
47	33. 0	32. 9	32. 7	32. 5	87	66. 9	66. 7	66. 4	66. 1
48	33. 9	33. 8	33. 6	33. 4	88	67. 7	67. 5	67. 2	66. 9
49	34. 8	34. 6	34. 4	34. 2	89	68. 5	68. 3	68. 1	67. 8
50	35. 6	35. 4	35. 2	35. 0	90	69. 3	69. 1	68. 9	68. 6

TABLE 94.—*Ratio of levulose to total sugar from the Lane and Eynon titration and Nyns "apparent" levulose*—Continued

$\frac{T \times l}{100}$	$T=15$	$T=25$	$T=35$	$T=45$	$\frac{T \times l}{100}$	$T=15$	$T=25$	$T=35$	$T=45$
91	70. 2	70. 0	69. 7	69. 4	111	86. 7	86. 4	86. 0	85. 7
92	71. 0	70. 8	70. 6	70. 3	112	87. 5	87. 2	86. 8	86. 5
93	71. 9	71. 7	71. 4	71. 1	113	88. 3	88. 0	87. 6	87. 3
94	72. 7	72. 5	72. 3	72. 0	114	89. 1	88. 8	88. 4	88. 1
95	73. 5	73. 3	73. 1	72. 8	115	90. 0	89. 6	89. 3	88. 9
96	74. 3	74. 2	73. 9	73. 6	116	90. 8	90. 4	90. 1	89. 7
97	75. 2	75. 0	74. 7	74. 4	117	91. 6	91. 3	91. 0	90. 6
98	76. 0	75. 8	75. 6	75. 3	118	92. 4	92. 1	92. 8	91. 4
99	76. 8	76. 6	76. 4	76. 1	119	93. 2	92. 9	92. 6	92. 2
100	77. 6	77. 4	77. 2	76. 9	120	94. 0	93. 7	93. 4	93. 0
101	78. 5	78. 2	78. 0	77. 7	121	94. 8	94. 5	94. 2	93. 8
102	79. 3	79. 0	78. 8	78. 5	122	95. 6	95. 3	95. 0	94. 6
103	80. 1	79. 9	79. 6	79. 3	123	96. 4	96. 1	95. 8	95. 4
104	81. 0	80. 7	80. 4	80. 1	124	97. 3	97. 0	96. 6	96. 2
105	81. 8	81. 5	81. 2	80. 9	125	98. 1	97. 8	97. 4	97. 0
106	82. 6	82. 3	82. 0	81. 7	126	98. 9	98. 6	98. 2	97. 8
107	83. 5	83. 2	82. 8	82. 5	127	99. 7	99. 4	99. 0	98. 6
108	84. 3	84. 0	83. 6	83. 3					
109	85. 1	84. 8	84. 4	84. 1					
110	85. 9	85. 6	85. 2	84. 9					

TABLE 95.—*Ratio of levulose to total sugar from the Lane and Eynon titration and the polarization by the Mathews formula*

[The table gives the percentage ratio (R) of levulose to total reducing sugar calculated from the Lane and Eynon titration and the direct polarization at 20° C. P is the polarization in °S; T is the corrected Lane and Eynon titer; D is the number of volumes to which one volume of the solution polarized was diluted for the titration; and f is the factor used for correcting the percentage ratio found in the table. This correction is given by $f \times D/T$ and is to be added algebraically.

The table can be used when the polarization is made at a temperature other than 20° C by using the temperature coefficient, $\Delta R/\Delta t°$. When the temperature is $t°$, the correction is $(\Delta R/\Delta t°)$ $(t° - 20°)$, and is to be added algebraically to the ratio.]

$\frac{P.T}{D}$	$T=15$	$T=25$	$T=35$	$T=45$	f	$\frac{\Delta R}{\Delta t°}$	$\frac{P.T}{D}$	$T=15$	$T=25$	$T=35$	$T=45$	f	$\frac{\Delta R}{\Delta t°}$
37	−0.6	−0.4	−0.3	−0.2	0.29	0	−18	52.2	52.2	52.1	52.1	−.35	.23
36	+0.4	+0.5	+0.7	+0.8	.28	0	−19	53.2	53.1	53.1	53.0	−.36	.23
35	1.4	1.5	1.6	1.7	.27	0.01	−20	54.2	54.1	54.0	54.0	−.37	.24
34	2.3	2.4	2.6	2.7	.26	.01	−21	55.1	55.0	55.0	54.9	−.38	.24
33	3.3	3.4	3.5	3.6	.24	.02	−22	56.1	56.0	56.0	55.9	−.39	.24
32	4.2	4.4	4.5	4.6	.23	.02	−23	57.0	57.0	56.9	56.8	−.40	.25
31	5.2	5.3	5.4	5.5	.22	.02	−24	58.0	57.9	57.9	57.8	−.42	.25
30	6.2	6.3	6.4	6.5	.21	.03	−25	59.0	58.9	58.8	58.7	−.43	.26
29	7.1	7.2	7.3	7.4	.20	.03	−26	59.9	59.8	59.8	59.7	−.44	.26
28	8.1	8.2	8.3	8.4	.19	.04	−27	60.9	60.8	60.7	60.6	−.45	.27
27	9.0	9.1	9.2	9.3	.18	.04	−28	61.8	61.7	61.7	61.6	−.46	.27
26	10.0	10.1	10.2	10.3	.16	.04	−29	62.8	62.7	62.6	62.5	−.47	.27
25	11.0	11.1	11.1	11.2	.15	.05	−30	63.8	63.7	63.6	63.5	−.49	.28
24	11.9	12.0	12.1	12.2	.14	.05							
23	12.9	13.0	13.1	13.1	.13	.06	−31	64.7	64.6	64.5	64.4	−.50	.28
							−32	65.7	65.6	65.5	65.4	−.51	.29
22	13.8	13.9	14.0	14.1	.12	.06	−33	66.6	66.5	66.4	66.3	−.52	.29
21	14.8	14.9	15.0	15.0	.11	.07	−34	67.6	67.5	67.4	67.3	−.53	.29
20	15.8	15.8	15.9	16.0	.09	.07							
19	16.7	16.8	16.9	16.9	.08	.07	−35	68.6	68.4	68.3	68.2	−.54	.30
18	17.7	17.7	17.8	17.9	.07	.08	−36	69.5	69.4	69.3	69.2	−.56	.30
							−37	70.5	70.3	70.2	70.1	−.57	.31
17	18.6	18.7	18.8	18.8	.06	.08	−38	71.4	71.3	71.2	71.1	−.58	.31
16	19.6	19.6	19.7	19.8	.05	.09	−39	72.4	72.3	72.1	72.0	−.59	.32
15	20.6	20.6	20.7	20.7	.04	.09							
14	21.5	21.6	21.6	21.7	.02	.10	−40	73.4	73.2	73.1	73.0	−.60	.32
							−41	74.3	74.2	74.1	73.9	−.61	.32
13	22.5	22.5	22.6	22.6	.01	.10	−42	75.3	75.1	75.0	74.9	−.63	.33
12	23.4	23.5	23.5	23.6	.00	.10	−43	76.2	76.1	76.0	75.8	−.64	.33
11	24.4	24.4	24.5	24.5	−.01	.11	−44	77.2	77.0	76.9	76.8	−.65	.34
10	25.4	25.4	25.4	25.5	−.02	.11							
							−45	78.2	78.0	77.9	77.7	−.66	.34
9	26.3	26.4	26.4	26.4	−.03	.12	−46	79.1	79.0	78.8	78.7	−.67	.34
8	27.3	27.3	27.3	27.4	−.05	.12	−47	80.1	79.9	79.8	79.6	−.68	.35
7	28.2	28.3	28.3	28.3	−.06	.12	−48	81.0	80.9	80.7	80.6	−.69	.35
6	29.2	29.2	29.3	29.3	−.07	.13	−49	82.0	81.8	81.7	81.5	−.71	.36
5	30.2	30.2	30.2	30.2	−.08	.13	−50	83.0	82.8	82.6	82.5	−.72	.36
4	31.1	31.1	31.2	31.2	−.09	.14	−51	83.9	83.7	83.6	83.4	−.73	.37
3	32.1	32.1	32.1	32.1	−.10	.14	−52	84.9	84.7	84.5	84.4	−.74	.37
2	33.0	33.0	33.1	33.1	−.11	.14	−53	85.8	85.7	85.5	85.3	−.75	.37
1	34.0	34.0	34.0	34.0	−.13	.15	−54	86.8	86.6	86.4	86.3	−.76	.38
0	35.0	35.0	35.0	35.0	−.14	.15							
−1	35.9	35.9	35.9	35.9	−.15	.16	−55	87.8	87.6	87.4	87.2	−.78	.38
−2	36.9	36.9	36.9	36.9	−.16	.16	−56	88.7	88.5	88.3	88.2	−.79	.39
−3	37.8	37.8	37.8	37.8	−.17	.17	−57	89.7	89.5	89.3	89.1	−.80	.39
							−58	90.6	90.4	90.3	90.1	−.81	.39
−4	38.8	38.8	38.8	38.8	−.18	.17							
−5	39.8	39.8	39.7	39.7	−.20	.17	−59	91.6	91.4	91.2	91.0	−.82	.40
−6	40.7	40.7	40.7	40.7	−.21	.18	−60	92.6	92.3	92.2	92.0	−.83	.40
−7	41.7	41.7	41.6	41.6	−.22	.18	−61	93.5	93.3	93.1	92.9	−.85	.41
−8	42.6	42.6	42.6	42.6	−.23	.19	−62	94.5	94.3	94.1	93.9	−.86	.41
−9	43.6	43.6	43.6	43.5	−.24	.19	−63	95.4	95.2	95.0	94.8	−.87	.42
−10	44.6	44.5	44.5	44.5	−.25	.19	−64	96.4	96.2	96.0	95.8	−.88	.42
−11	45.5	45.5	45.5	45.4	−.27	.20	−65	97.4	97.1	96.9	96.7	−.89	.42
−12	46.5	46.4	46.4	46.4	−.28	.20	−66	98.3	98.1	97.9	97.7	−.90	.43
−13	47.4	47.4	47.4	47.3	−.29	.21							
−14	48.4	48.4	48.3	48.3	−.30	.21	−67	99.3	99.0	98.8	98.6	−.92	.43
−15	49.4	49.3	49.3	49.2	−.31	.22	−68	100.2	100.0	99.8	99.6	−.93	.44
−16	50.3	50.3	50.2	50.2	−.32	.22	−69	101.2	101.0	100.7	100.5	−.94	.44
−17	51.3	51.2	51.2	51.1	−.34	.22	−70	102.2	101.9	101.7	101.5	−.95	.44

TABLE 96.—*Schoorl method for the determination of reducing sugar in cane molasses*

Copper	Reducing sugars				
	Pol. 10°	Pol. 20°	Pol. 30°	Pol. 40°	Pol. 60°
mg	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
100	8. 70	8. 60	8. 57	8. 55	8. 53
120	10. 44	10. 36	10. 32	10. 28	10. 28
140	12. 20	12. 11	12. 09	12. 06	12. 04
160	14. 03	13. 95	13. 89	13. 87	13. 81
180	15. 84	15. 78	15. 69	15. 66	15. 60
200	17. 70	17. 63	17. 53	17. 50	17. 43
220	19. 54	19. 50	19. 44	19. 36	19. 25
240	21. 40	21. 36	21. 28	21. 20	21. 12
260	23. 27	23. 22	23. 13	23. 05	22. 97
280	25. 16	25. 12	25. 02	24. 91	24. 83
300	27. 05	27. 00	26. 95	26. 90	26. 80
320	29. 07	29. 01	28. 95	28. 90	28. 80
340	31. 11	31. 05	30. 98	30. 91	30. 77
360	33. 18	33. 11	33. 04	32. 96	32. 82
380	35. 28	35. 15	35. 08	35. 01	34. 89
400	37. 40	37. 27	37. 20	37. 13	37. 00

TABLE 97.—*Luff and Schoorl method for the determination of invert sugar in cane sugar*

Thiosulfate, 0.1 N	Invert sugar in reaction mixtures containing—			
	No sucrose	1.25 g of sucrose	2.5 g of sucrose	5 g of sucrose
ml	*mg*	*mg*	*mg*	*mg*
0. 0	0. 00			
. 4	1. 40	1. 00	0. 60	0. 15
. 5	1. 75	1. 30	. 90	. 45
1. 0	3. 50	2. 90	2. 50	2. 00
2. 0	6. 55	5. 90	5. 50	5. 00
4. 0	12. 55	11. 90	11. 50	11. 00
6. 0	18. 60	18. 00	17. 50	17. 00
8. 0	24. 70	24. 10	23. 55	23. 00
10. 0	30. 85	30. 25	29. 75	29. 05
12. 0	37. 10	36. 55	36. 15	35. 30
14. 0	43. 50	42. 95	42. 50	41. 70
16. 0	50. 20	49. 65	49. 15	48. 30

TABLE 98.—*Somogyi*[1] *dextrose–thiosulfate equivalents*

[Amounts of dextrose corresponding to titration values when 5 ml of solution and 5 ml of copper reagent (modified) are heated in a water bath for 15 minutes]

Thiosulfate, 0.005 *N*	Tenths of 1 ml of 0.005 *N* sodium thiosulfate									
	0	1	2	3	4	5	6	7	8	9
	Milligrams of dextrose in 5 ml of solution									
ml										
0	------	------	0. 11	0. 12	0. 13	0. 15	0. 16	0. 17	0. 18	0. 20
1	. 21	. 22	. 23	. 25	. 26	. 27	. 28	. 29	. 31	. 32
2	. 33	. 34	. 35	. 36	. 38	. 39	. 40	. 41	. 42	. 43
3	. 45	. 46	. 47	. 485	. 495	. 505	. 515	. 530	. 540	. 550
4	. 565	. 575	. 585	. 595	. 605	. 620	. 630	. 640	. 650	. 660
5	. 670	. 685	. 695	. 705	. 715	. 730	. 740	. 750	. 760	. 770
6	. 785	. 795	. 805	. 815	. 825	. 840	. 850	. 860	. 870	. 880
7	. 895	. 905	. 915	. 925	. 935	. 950	. 960	. 970	. 980	. 995
8	1. 005	1. 015	1. 025	1. 035	1. 050	1. 060	1. 070	1. 080	1. 090	1. 105
9	1. 115	1. 125	1. 135	1. 115	1. 116	1. 117	1. 185	1. 195	1. 205	1. 215
10	1. 225	1. 24	1. 25	1. 26	1. 27	1. 28	1. 295	1. 305	1. 315	1. 325
11	1. 335	1. 35	1. 36	1. 37	1. 38	1. 395	1. 405	1. 415	1. 425	1. 44
12	1. 450	1. 460	1. 470	1. 480	1. 495	1. 505	1. 515	1. 525	1. 54	1. 55
13	1. 560	1. 570	1. 580	1. 590	1. 605	1. 615	1. 63	1. 640	1. 650	1. 660
14	1. 670	1. 685	1. 695	1. 705	1. 715	1. 725	1. 735	1. 750	1. 760	1. 170
15	1. 780	1. 795	1. 805	1. 815	1. 825	1. 835	1. 850	1. 860	1. 870	1. 880
16	1. 89	1. 905	1. 915	1. 930	1. 940	1. 950	1. 960	1. 970	1. 98	1. 990
17	2. 00	------	------	------	------	------	------	------	------	------

[1] M. Somogyi, J. Biol. Chem. **70**, 607 (1926). 1 ml of 0.005 *N* thiosulfate equals 0.318 mg of copper.

TABLE 99.—*Hagedorn and Jensen dextrose equivalents*

Sodium thio-sulfate, 0.005 *N*	Hundredths of 1 ml of 0.005 *N* sodium thiosulfate									
	.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
	Milligrams of dextrose									
ml										
0. 0	0. 385	0. 382	0. 379	0. 376	0. 373	0. 370	0. 367	0. 364	0. 361	0. 358
. 1	. 355	. 352	. 350	. 348	. 345	. 343	. 341	. 338	. 336	. 333
. 2	. 331	. 329	. 327	. 325	. 323	. 321	. 318	. 316	. 314	. 312
. 3	. 310	. 308	. 306	. 304	. 302	. 300	. 298	. 296	. 294	. 292
. 4	. 290	. 288	. 286	. 284	. 282	. 280	. 278	. 276	. 274	. 272
. 5	. 270	. 268	. 266	. 264	. 262	. 260	. 259	. 257	. 255	. 253
. 6	. 251	. 249	. 247	. 245	. 243	. 241	. 240	. 238	. 236	. 234
. 7	. 232	. 230	. 228	. 226	. 224	. 222	. 221	. 219	. 217	. 215
. 8	. 213	. 211	. 209	. 208	. 206	. 204	. 202	. 200	. 199	. 197
. 9	. 195	. 193	. 191	. 190	. 188	. 186	. 184	. 182	. 181	. 179
1. 0	. 177	. 175	. 173	. 172	. 170	. 168	. 166	. 164	. 163	. 161
1. 1	. 159	. 157	. 155	. 154	. 152	. 150	. 148	. 146	. 145	. 143
1. 2	. 141	. 139	. 138	. 136	. 134	. 132	. 131	. 129	. 127	. 125
1. 3	. 124	. 122	. 120	. 119	. 117	. 115	. 113	. 111	. 110	. 108
1. 4	. 106	. 104	. 102	. 101	. 099	. 097	. 095	. 093	. 092	. 090
1. 5	. 088	. 086	. 084	. 083	. 081	. 079	. 077	. 075	. 074	. 072
1. 6	. 070	. 068	. 066	. 065	. 063	. 061	. 059	. 057	. 056	. 054
1. 7	. 052	. 050	. 048	. 047	. 045	. 043	. 041	. 039	. 038	. 036
1. 8	. 034	. 032	. 031	. 029	. 027	. 025	. 024	. 022	. 020	. 019
1. 9	. 017	. 015	. 014	. 012	. 010	. 008	. 007	. 005	. 003	. 002

TABLE 100.—*Pot method of Main for invert sugar*

[Using Fehling solution, Soxhlet modification; time of heating in boiling water, 5 min.; indicator, 2 drops of 1-percent methylene blue in each tube]

Sucrose g/100 ml	0 to 1	0	1	1	1	2. 5	2. 5	5	10
Fehling solution, ml	20	10	10	5	2. 5	5	2. 5	2. 5	2. 5
Solution required for reduction	Invert sugar/100 ml			Invert sugar					
ml	*g*	*g*	*g*	%	%	%	%	%	%
15	0. 648	0. 330	0. 325	16. 6	8. 58	6. 60	3. 35	1. 61	0. 742
16	. 608	. 309	. 306	15. 6	8. 06	6. 15	3. 12	1. 50	. 698
17	. 574	. 290	. 288	14. 7	7. 60	5. 78	2. 94	1. 41	. 658
18	. 543	. 274	. 272	13. 9	7. 18	5. 46	2. 78	1. 33	. 620
19	. 514	. 260	. 258	13. 2	6. 80	5. 17	2. 63	1. 26	. 584
20	. 487	. 248	. 246	12. 5	6. 45	4. 90	2. 49	1. 19	. 551
21	. 462	. 237	. 235	11. 9	6. 14	4. 66	2. 37	1. 13	. 520
22	. 440	. 226	. 224	11. 4	5. 86	4. 45	2. 26	1. 08	. 493
23	. 420	. 216	. 214	10. 9	5. 60	4. 26	2. 16	1. 03	. 470
24	. 402	. 206	. 205	10. 5	5. 36	4. 08	2. 06	. 975	. 450
25	. 387	. 198	. 197	10. 1	5. 14	3. 90	1. 98	. 935	. 432
26	. 374	. 190	. 190	9. 70	4. 94	3. 76	1. 90	. 902	. 416
27	. 361	. 183	. 183	9. 34	4. 76	3. 62	1. 82	. 870	. 400
28	. 349	. 177	. 177	9. 00	4. 58	3. 49	1. 75	. 840	. 386
29	. 337	. 171	. 171	8. 70	4. 42	3. 37	1. 69	. 812	. 373
30	. 326	. 165	. 165	8. 40	4. 28	3. 26	1. 63	. 788	. 361
31	. 316	. 160	. 160	8. 15	4. 14	3. 15	1. 57	. 760	. 349
32	. 306	. 155	. 155	7. 90	4. 01	3. 04	1. 52	. 735	. 338
33	. 297	. 151	. 151	7. 65	3. 89	2. 95	1. 47	. 710	. 328
34	. 288	. 147	. 147	7. 45	3. 78	2. 87	1. 43	. 690	. 319
35	. 280	. 143	. 143	7. 25	3. 68	2. 80	1. 40	. 670	. 312

323414°—42——40

TABLE 101.—*Pot method of Main for small quantities of invert sugar* [1]

[Using a Fehling solution containing potassium ferrocyanide; indicator, 2 drops of 1-percent methylene blue in each tube]

Sucrose, g/100 ml	5	10	20	20	20	30	20	30
L. F. S. extra alkaline, ml	4	4	4	2	1	1	1	1
Time of heating in boiling water, min	5	5	5	5	5	5	10	10
Solution required for reduction	Invert sugar/100 ml				Invert sugar			
ml	*g*	*g*	*g*	*g*	%	%	%	%
15	0.832	0.384	0.182	0.0878	0.0390	0.0265	0.0106	0.0085
16	.779	.356	.170	.0828	.0381	.0251	.0095	.0071
17	.740	.338	.161	.0783	.0368	.0229	.0086	.0060
18	.704	.324	.153	.0739	.0348	.0208	.0079	.0052
19	.670	.310	.146	.0697	.0323	.0191	.0074	.0045
20	.638	.296	.140	.0660	.0299	.0177	.0069	.0040
21	.608	.283	.134	.0628	.0279	.0166	.0065	.0035
22	.581	.270	.128	.0600	.0262	.0158	.0061	.0031
23	.556	.256	.123	.0575	.0249	.0151	.0058	.0028
24	.533	.243	.118	.0553	.0237	.0145	.0055	.0025
25	.512	.232	.113	.0530	.0226	.0139	.0052	------
26	.493	.222	.109	.0510	.0216	.0133	.0050	.0020
27	.476	.215	.105	.0491	.0207	.0128	.0047	------
28	.459	.209	.101	.0473	.0198	.0123	.0045	.0015
29	.444	.203	.097	.0455	.0190	.0119	.0043	------
30	.429	.198	.0935	.0438	.0182	.0114	.0041	.0010
31	.415	.193	.090	.0424	.0175	.0109	------	------
32	.402	.189	.0865	.0408	.0168	.0105	------	------
33	.390	.185	.083	.0393	.0162	.0101	------	------
34	.380	.181	.080	.0380	.0156	.0097	------	------
35	.370	.178	.0765	.0369	.0151	.0094	------	------

[1] Int. Sugar J. **34**, 213 (1932).

TABLE 102.—*Sichert and Bleyer modification of the Barfoed copper acetate method for hexoses* [1]

Permanganate, 0.1 *N* titer	Tenths of 1 ml of 0.1 *N* permanganate									
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	Milligrams of dextrose									
ml										
10	26. 5	26. 8	27. 1	27. 4	27. 8	28. 1	28. 4	28. 7	29. 0	29. 3
11	29. 7	30. 0	30. 4	30. 7	31. 1	31. 5	31. 8	32. 2	32. 6	32. 9
12	33. 3	33. 7	34. 1	34. 5	34. 9	35. 4	35. 8	36. 2	36. 6	37. 0
13	37. 4	37. 9	38. 4	38. 8	39. 3	39. 8	40. 2	40. 7	41. 2	41. 7
14	42. 2	42. 7	43. 2	43. 8	44. 3	44. 9	45. 4	46. 0	46. 5	47. 0
15	47. 6	48. 2	48. 8	49. 4	50. 1	50. 7	51. 3	51. 9	52. 5	53. 2
16	53. 8	54. 5	55. 2	55. 9	56. 6	57. 3	58. 0	58. 7	59. 4	60. 2
17	60. 9	61. 7	62. 5	63. 3	64. 1	64. 9	65. 7	66. 5	67. 4	68. 2
18	69. 0	69. 9	70. 9	71. 9	72. 8	73. 8	74. 8	75. 7	76. 7	77. 6
19	78. 6	79. 6	80. 7	81. 7	82. 7	83. 7	84. 8	85. 8	86. 8	87. 8
20	88. 9	90. 0	91. 2	92. 3	93. 5	94. 7	96. 0	97. 2	98. 5	99. 7

[1] The table may be interpolated for hundredths of a milliliter, but should *not* be extrapolated.

TABLE 103.—*Van der Haar mucic-acid equivalents of galactose*

Galactose	Mucic acid obtained when sample contains—		Galactose	Mucic acid obtained when sample contains—	
	Galactose	Galactose+sucrose to equal 1,000 mg		Galactose	Galactose+sucrose to equal 1,000 mg
mg	*mg*	*mg*	*mg*	*mg*	*mg*
0	−4	−4	500	366	360
10	+0. 8	+2. 4	510	374. 9	368
20	5. 6	8. 8	520	383. 8	376
30	10. 4	15. 2	530	392. 7	384
40	15. 2	21. 6	540	401. 6	392
50	20	28. 0	550	410. 5	400
60	27	34. 9	560	419. 4	408
70	34	41. 8	570	428. 3	416
80	41	48. 7	580	437. 2	424
90	48	55. 6	590	446. 1	432
100	55	62. 5	600	455	440
110	64	70. 0	610	462	447
120	73	77. 5	620	469	454
130	82	85. 0	630	476	461
140	91	92. 5	640	483	468
150	100	100. 0	650	490	475
160	108. 4	106. 6	660	497	483
170	116. 8	113. 2	670	504	491
180	125. 2	119. 8	680	511	499
190	133. 6	126. 4	690	518	507
200	142. 0	133. 0	700	525	515
210	149. 6	139. 4	710	534	523
220	157. 2	145. 8	720	543	531
230	164. 8	152. 2	730	552	539
240	172. 4	158. 6	740	561	547
250	180	165	750	570	555
260	187	173	760	579	564
270	194	181	770	588	573
280	201	189	780	597	582
290	208	197	790	606	591
300	215	205	800	615	600
310	223. 1	212	810	623	609
320	231. 2	219	820	631	618
330	239. 3	226	830	639	627
340	247. 4	233	840	647	636
350	255. 5	240	850	655	645
360	263. 6	248. 8	860	663	654
370	271. 7	257. 6	870	671	663
380	279. 8	166. 4	880	679	672
390	287. 9	275. 2	890	688	681
400	296	284. 0	900	695	690
410	303	292. 2	910	703. 5	699
420	310	300. 4	920	712	708
430	317	308. 6	930	720. 5	717
440	324	316. 8	940	729	726
450	331	325	950	737. 5	735
460	338	332	960	746	744
470	345	339	970	754. 5	753
480	352	346	980	763	762
490	359	353	990	771. 5	771
			1, 000	780	780

TABLE 104.—*Steinhoff table for estimation of dextrose, maltose, and dextrin*

0.1 *N* Iodine	1	2	3	4
	Analysis *A*	Analysis *B*	Maltose by difference	Analysis *C*
ml.	*mg.*	*mg.*	*mg.*	*mg.*
1	6. 1	1. 9	5. 0	3. 2
2	8. 6	2. 7	10. 5	6. 3
3	11. 2	3. 6	16. 0	9. 4
4	13. 4	4. 3	21. 5	12. 6
5	15. 6	4. 9	27. 0	15. 9
6	18. 1	5. 7	32. 5	19. 2
7	20. 5	6. 4	38. 0	22. 4
8	23. 2	7. 3	43. 5	25. 6
9	25. 8	8. 1	49. 0	28. 9
10	28. 4	8. 9	55. 0	32. 3
11	31. 2	9. 7	60. 5	35. 7
12	34. 2	10. 6	66. 0	39. 0
13	37. 3	11. 5	72. 0	42. 4
14	40. 5	12. 4	78. 0	45. 8
15	46. 8	14. 3	83. 5	49. 3
16	52. 8	16. 0	89. 0	52. 8
17	58. 6	17. 7	95. 0	56. 3
18	66. 0	19. 8	101. 0	59. 8
19	73. 4	21. 8	107. 0	63. 3
20	80. 0	23. 4	112. 5	66. 9
21	88. 4	25. 4	118. 5	70. 7
22	96. 2	27. 3	124. 5	74. 5
23	----------	----------	130. 5	78. 5
24	----------	----------	136. 5	82. 6
25	----------	----------	142. 5	86. 6
26	----------	----------	148. 5	90. 7
27	----------	----------	154. 5	94. 8

TABLE 105.—*Kröber table for the determination of pentoses and pentosans*

Furfural phloroglucide	Furfural	Arabinose	Araban	Xylose	Xylan	Pentose	Pentosan
g	*g*	*g*	*g*	*g*	*g*	*g*	*g*
0.030	0.0182	0.0391	0.0344	0.0324	0.0285	0.0358	0.0315
.032	.0193	.0413	.0363	.0342	.0301	.0378	.0333
.034	.0203	.0435	.0383	.0361	.0317	.0398	.0350
.036	.0214	.0457	.0402	.0379	.0334	.0418	.0368
.038	.0224	.0479	.0422	.0398	.0350	.0439	.0386
.040	.0235	.0501	.0441	.0416	.0366	.0459	.0404
.042	.0245	.0523	.0460	.0434	.0382	.0479	.0422
.044	.0255	.0545	.0480	.0452	.0398	.0499	.0440
.046	.0266	.0567	.0499	.0471	.0414	.0519	.0457
.048	.0276	.0589	.0519	.0489	.0430	.0539	.0475
.050	.0286	.0611	.0538	.0507	.0446	.0559	.0492
.052	.0297	.0633	.0557	.0525	.0462	.0579	.0510
.054	.0307	.0655	.0576	.0543	.0478	.0599	.0528
.056	.0318	.0677	.0596	.0562	.0494	.0620	.0546
.058	.0328	.0699	.0615	.0580	.0510	.0640	.0564
.060	.0338	.0721	.0634	.0598	.0526	.0660	.0581
.062	.0349	.0743	.0653	.0616	.0542	.0680	.0599
.064	.0359	.0765	.0673	.0635	.0558	.0700	.0617
.066	.0370	.0787	.0692	.0653	.0575	.0720	.0634
.068	.0380	.0809	.0712	.0672	.0591	.0741	.0652
.070	.0390	.0831	.0731	.0690	.0607	.0761	.0670
.072	.0401	.0853	.0750	.0708	.0623	.0781	.0688
.074	.0411	.0875	.0770	.0726	.0639	.0801	.0706
.076	.0422	.0897	.0789	.0745	.0655	.0821	.0722
.078	.0432	.0919	.0809	.0763	.0671	.0841	.0740
.080	.0442	.0941	.0828	.0781	.0687	.0861	.0758
.082	.0453	.0963	.0847	.0799	.0703	.0881	.0776
.084	.0463	.0985	.0867	.0817	.0719	.0901	.0794
.086	.0474	.1007	.0886	.0836	.0735	.0922	.0812
.088	.0484	.1029	.0906	.0854	.0751	.0942	.0830
.090	.0494	.1051	.0925	.0872	.0767	.0962	.0847
.092	.0505	.1073	.0944	.0890	.0783	.0982	.0865
.094	.0515	.1095	.0964	.0909	.0800	.1002	.0883
.096	.0525	.1117	.0983	.0927	.0816	.1022	.0899
.098	.0536	.1139	.1003	.0946	.0832	.1043	.0917
.100	.0546	.1161	.1022	.0964	.0848	.1063	.0935
.102	.0557	.1182	.1041	.0982	.0864	.1083	.0953
.104	.0567	.1204	.1060	.1000	.0880	.1103	.0971
.106	.0577	.1226	.1080	.1019	.0896	.1123	.0988
.108	.0588	.1248	.1099	.1037	.0912	.1143	.1006
.110	.0598	.1270	.1118	.1055	.0928	.1163	.1023
.112	.0608	.1292	.1137	.1073	.0944	.1183	.1041
.114	.0619	.1314	.1156	.1091	.0960	.1203	.1059
.116	.0619	.1336	.1176	.1110	.0976	.1223	.1076
.118	.0640	.1358	.1195	.1128	.0992	.1243	.1094
.120	.0650	.1380	.1214	.1146	.1008	.1263	.1111
.122	.0660	.1402	.1233	.1164	.1024	.1283	.1129
.124	.0671	.1424	.1253	.1182	.1040	.1303	.1147
.126	.0681	.1446	.1272	.1201	.1057	.1324	.1165
.128	.0691	.1468	.1292	.1219	.1073	.1344	.1183
.130	.0702	.1490	.1311	.1237	.1089	.1364	.1201
.132	.0712	.1512	.1330	.1255	.1105	.1384	.1219
.134	.0723	.1534	.1350	.1273	.1121	.1404	.1236
.136	.0733	.1556	.1369	.1292	.1137	.1424	.1253
.138	.0743	.1578	.1389	.1310	.1153	.1444	.1271
.140	.0754	.1600	.1408	.1328	.1169	.1464	.1288
.142	.0764	.1622	.1427	.1346	.1185	.1484	.1306
.144	.0774	.1644	.1447	.1364	.1201	.1504	.1324
.146	.0785	.1666	.1466	.1383	.1217	.1525	.1342
.148	.0795	.1688	.1486	.1401	.1233	.1545	.1360
.150	.0805	.1710	.1505	.1419	.1249	.1565	.1377
.152	.0816	.1732	.1524	.1437	.1265	.1585	.1395
.154	.0826	.1754	.1544	.1455	.1281	.1605	.1413
.156	.0837	.1776	.1563	.1474	.1297	.1625	.1430
.158	.0847	.1798	.1583	.1492	.1313	.1645	.1448
.160	.0857	.1820	.1602	.1510	.1329	.1665	.1465
.162	.0868	.1842	.1621	.1528	.1345	.1685	.1483
.164	.0878	.1864	.1640	.1546	.1361	.1705	.1501
.166	.0888	.1886	.1660	.1565	.1377	.1726	.1519
.168	.0899	.1908	.1679	.1583	.1393	.1746	.1537

TABLE 105.—*Kröber table for the determination of pentoses and pentosans*—Con.

Furfural phloroglucide	Furfural	Arabinose	Araban	Xylose	Xylan	Pentose	Pentosan
g	*g*	*g*	*g*	*g*	*g*	*g*	*g*
.170	.0909	.1930	.1698	.1601	.1409	.1766	.1554
.172	.0920	.1952	.1717	.1619	.1425	.1786	.1572
.174	.0930	.1974	.1736	.1637	.1441	.1806	.1590
.176	.0940	.1996	.1756	.1656	.1457	.1826	.1607
.178	.0951	.2018	.1775	.1674	.1473	.1846	.1625
.180	.0961	.2039	.1794	.1692	.1489	.1866	.1642
.182	.0971	.2061	.1813	.1710	.1505	.1886	.1660
.184	.0982	.2082	.1832	.1728	.1521	.1906	.1678
.186	.0992	.2104	.1851	.1747	.1537	.1926	.1695
.188	.1003	.2126	.1870	.1765	.1553	.1946	.1712
.190	.1013	.2147	.1889	.1783	.1569	.1965	.1729
.192	.1023	.2168	.1908	.1801	.1585	.1985	.1747
.194	.1034	.2190	.1927	.1819	.1601	.2005	.1764
.196	.1044	.2212	.1946	.1838	.1617	.2025	.1782
.198	.1054	.2233	.1965	.1856	.1633	.2045	.1800
.200	.1065	.2255	.1984	.1874	.1649	.2065	.1817
.202	.1075	.2276	.2003	.1892	.1665	.2085	.1835
.204	.1085	.2298	.2022	.1910	.1681	.2105	.1853
.206	.1096	.2320	.2041	.1929	.1697	.2125	.1869
.208	.1106	.2341	.2060	.1947	.1713	.2144	.1887
.210	.1116	.2363	.2079	.1965	.1729	.2164	.1904
.212	.1127	.2384	.2098	.1984	.1745	.2184	.1922
.214	.1137	.2406	.2117	.2002	.1761	.2204	.1940
.216	.1147	.2428	.2136	.2020	.1778	.2224	.1957
.218	.1158	.2449	.2155	.2038	.1794	.2244	.1974
.220	.1168	.2471	.2174	.2057	.1810	.2264	.1992
.222	.1178	.2492	.2193	.2075	.1826	.2284	.2010
.224	.1189	.2514	.2212	.2093	.1842	.2304	.2028
.226	.1199	.2536	.2232	.2111	.1858	.2324	.2046
.228	.1209	.2557	.2251	.2130	.1874	.2344	.2063
.230	.1220	.2579	.2270	.2148	.1890	.2364	.2081
.232	.1230	.2600	.2289	.2166	.1906	.2383	.2097
.234	.1240	.2622	.2308	.2184	.1922	.2403	.2115
.236	.1251	.2644	.2327	.2202	.1938	.2423	.2132
.238	.1261	.2665	.2346	.2220	.1954	.2443	.2150
.240	.1271	.2687	.2365	.2239	.1970	.2463	.2168
.242	.1281	.2708	.2384	.2257	.1986	.2483	.2185
.244	.1292	.2730	.2403	.2275	.2002	.2503	.2203
.246	.1302	.2752	.2422	.2293	.2018	.2523	.2220
.248	.1312	.2773	.2441	.2311	.2034	.2543	.2238
.250	.1323	.2795	.2460	.2330	.2050	.2563	.2256
.252	.1333	.2816	.2479	.2348	.2066	.2582	.2272
.254	.1343	.2838	.2498	.2366	.2082	.2602	.2290
.256	.1354	.2860	.2517	.2384	.2098	.2622	.2307
.258	.1364	.2881	.2536	.2402	.2114	.2642	.2325
.260	.1374	.2903	.2555	.2420	.2130	.2662	.2342
.262	.1385	.2924	.2574	.2438	.2146	.2681	.2359
.264	.1395	.2946	.2593	.2456	.2162	.2701	.2377
.266	.1405	.2968	.2612	.2474	.2178	.2721	.2394
.268	.1416	.2989	.2631	.2492	.2194	.2741	.2412
.270	.1426	.3011	.2650	.2511	.2210	.2761	.2429
.272	.1436	.3032	.2669	.2529	.2226	.2781	.2447
.274	.1447	.3054	.2688	.2547	.2242	.2801	.2465
.276	.1457	.3076	.2707	.2565	.2258	.2821	.2482
.278	.1467	.3097	.2726	.2583	.2274	.2840	.2499
.280	.1478	.3119	.2745	.2602	.2290	.2861	.2517
.282	.1488	.3140	.2764	.2620	.2306	.2880	.2534
.284	.1498	.3162	.2783	.2638	.2322	.2900	.2552
.286	.1509	.3184	.2802	.2656	.2338	.2920	.2570
.288	.1519	.3205	.2821	.2674	.2354	.2940	.2587
.290	.1529	.3227	.2840	.2693	.2370	.2960	.2605
.292	.1540	.3248	.2859	.2711	.2386	.2980	.2622
.294	.1550	.3270	.2878	.2729	.2402	.3000	.2640
.296	.1560	.3292	.2897	.2747	.2418	.3020	.2658
.298	.1571	.3313	.2916	.2765	.2434	.3040	.2675
.300	.1581	.3335	.2935	.2784	.2450	.3060	.2693

TABLE 106.—*Apparent weight of water in air*

[This table gives the apparent weight for temperatures between 15° and 30° C, humidity 50 percent, unreduced barometer reading 76 cm, of certain volumes of water weighed with brass weights. The table may be conveniently employed to determine definite volumes of water for calibrating instruments. The air is assumed to be at the same temperature as the water]

Temperature	2,000 ml	1,000 ml	500 ml	400 ml	300 ml	250 ml	150 ml
° *C*	*g*	*g*	*g*	*g*	*g*	*g*	*g*
15	1996. 11	998. 05	499. 03	399. 22	299. 42	249. 51	149. 71
16	1995. 80	997. 90	498. 95	399. 16	299. 37	249. 48	149. 68
17	1995. 48	997. 74	498. 87	399. 10	299. 32	249. 43	149. 66
18	1995. 13	997. 56	498. 78	399. 03	299. 27	249. 39	149. 63
19	1994. 76	997. 38	498. 69	398. 95	299. 21	249. 34	149. 61
20	1994. 36	997. 18	498. 59	398. 87	299. 15	249. 30	149. 58
21	1993. 95	996. 97	498. 49	398. 79	299. 09	249. 24	149. 55
22	1993. 51	996. 76	498. 38	398. 70	299. 03	249. 19	149. 51
23	1993. 06	996. 53	498. 26	398. 61	298. 96	249. 13	149. 48
24	1992. 58	996. 29	498. 15	398. 52	298. 89	249. 07	149. 44
25	1992. 09	996. 04	498. 02	398. 42	298. 81	249. 01	149. 41
26	1991. 57	995. 79	497. 89	398. 31	298. 74	248. 95	149. 37
27	1991. 04	995. 52	497. 76	398. 21	298. 66	248. 88	149. 33
28	1990. 49	995. 24	497. 62	398. 10	298. 57	248. 81	149. 29
29	1989. 92	994. 96	497. 48	397. 98	298. 49	248. 74	149. 24
30	1989. 33	994. 66	497. 33	397. 87	298. 40	248. 67	149. 20

TABLE 107.—*Temperature correction for glass volumetric apparatus*

[This table gives the correction to be added to actual capacity (determined at certain temperatures) to give the capacity at the standard temperature, 20° C Conversely, by subtracting the corrections from the indicated capacity of an instrument standard at 20° C the corresponding capacity at other temperatures is obtained. The table assumes for the cubical coefficient of expansion of glass 0.000025 per degree centigrade. The coefficients of expansion of glasses used for volumetric instruments vary from 0.000023 to 0.000028]

Temperature	2,000 ml	1,000 ml	500 ml	400 ml	300 ml	250 ml
° *C*	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*
15	+0. 25	+0. 12	+0. 06	+0. 05	+0. 04	+0. 031
16	+. 20	+. 10	+. 05	+. 04	+. 03	+. 025
17	+. 15	+. 08	+. 04	+. 03	+. 02	+. 019
18	+. 10	+. 05	+. 02	+. 02	+. 02	+. 012
19	+. 05	+. 02	+. 01	+. 01	+ 01	+. 006
21	−. 05	−. 02	−. 01	−. 01	−. 01	−. 006
22	−. 10	−. 05	−. 02	−. 02	−. 02	−. 012
23	−. 15	−. 08	−. 04	−. 03	−. 02	−. 019
24	−. 20	−. 10	−. 05	−. 04	−. 03	−. 025
25	−. 25	−. 12	−. 06	−. 05	−. 04	−. 031
26	−. 30	−. 15	−. 08	−. 06	−. 04	−. 038
27	−. 35	−. 18	−. 09	−. 07	−. 05	−. 044
28	−. 40	−. 20	−. 10	−. 08	−. 06	−. 050
29	−. 45	−. 22	−. 11	−. 09	−. 07	−. 056
30	−. 50	−. 25	−. 12	− 10	−. 08	−. 062

TABLE 108.—*Reduction of weighings to vacuo*

The weight of a body in vacuo is determined by adding to its apparent weight in air a buoyancy correction equal to the weight of the air displaced by the difference in volume of the body weighed and the weights required to balance it on an equal-arm balance.

$$M=W+\rho\left(\frac{M}{d_1}-\frac{W}{d_2}\right)=W\frac{d_1}{d_2}\left(\frac{d_2-\rho}{d_1-\rho}\right)=W\frac{d_1}{d_1-\rho}\left(1-\frac{\rho}{d_2}\right)=$$
$$W[1+\frac{\rho}{d_2}\left(\frac{d_2-d_1}{d_1-\rho}\right)]=W+\frac{kW}{1000}=W\left(1+\frac{k}{1000}\right).$$

M = Weight in vacuo.
W = Apparent weight in air.
ρ = Density of air.
d_1 = Density of body.
d_2 = Density of weights.
ρ = 0.0012046 (table 29, BS Cir. C19).

Density of body weighed	Correction factor k, brass weights	Density of body weighed	Correction factor k, brass weights	Density of body weighed	Correction factor k, brass weights
g/ml		*g/ml*		*g/ml*	
0. 95	1. 1260	1. 19	0. 8697	1. 43	0. 6996
. 96	1. 1128	1. 20	. 8613	1. 44	. 6937
. 97	1. 0998	1. 21	. 8530	1. 45	. 6879
. 98	1. 0871	1. 22	. 8448	1. 46	. 6822
. 99	1. 0747	1. 23	. 8368	1. 47	. 6766
1. 00	1. 0625	1. 24	. 8289	1. 48	. 6711
1. 01	1. 0505	1. 25	. 8211	1. 49	. 6656
1. 02	1. 0388	1. 26	. 8134	1. 50	. 6602
1. 03	1. 0273	1. 27	. 8059	1. 51	. 6549
1. 04	1. 0160	1. 28	. 7984	1. 52	. 6496
1. 05	1. 0050	1. 29	. 7911	1. 53	. 6444
1. 06	0. 9941	1. 30	. 7839	1. 54	. 6393
1. 07	. 9835	1. 31	. 7769	1. 55	. 6343
1. 08	. 9731	1. 32	. 7699	1. 56	. 6293
1. 09	. 9628	1. 33	. 7630	1. 57	. 6243
1. 10	. 9527	1. 34	. 7562	1. 58	. 6195
1. 11	. 9428	1. 35	. 7496	1. 59	. 6147
1. 12	. 9331	1. 36	. 7430	1. 60	. 6099
1. 13	. 9236	1. 37	. 7365	1. 61	. 6052
1. 14	. 9142	1. 38	. 7291	1. 62	. 6006
1. 15	. 9050	1. 39	. 7238	1. 63	. 5961
1. 16	. 8960	1. 40	. 7176	1. 64	. 5915
1. 17	. 8871	1. 41	. 7115	1. 65	. 5871
1. 18	. 8783	1. 42	. 7055		

TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
0. 0	0. 99823	1. 00000	0. 00	5. 0	1. 01785	1. 01965	2. 79
. 1	. 99862	1. 00039	. 06	5. 1	1. 01825	1. 02005	2. 85
. 2	. 99901	1. 00078	. 11	5. 2	1. 01865	1. 02045	2. 91
. 3	. 99940	1. 00117	. 17	5. 3	1. 01905	1. 02085	2. 96
. 4	. 99979	1. 00155	. 22	5. 4	1. 01945	1. 02125	3. 02
. 5	1. 00017	1. 00194	. 28	5. 5	1. 01985	1. 02165	3. 07
. 6	1. 00056	1. 00233	. 34	5. 6	1. 02025	1. 02206	3. 13
. 7	1. 00095	1. 00272	. 39	5. 7	1. 02065	1. 02246	3. 18
. 8	1. 00134	1. 00311	. 45	5. 8	1. 02105	1. 02286	3. 24
. 9	1. 00173	1. 00350	. 51	5. 9	1. 02145	1. 02321	3. 30
1. 0	1. 00212	1. 00389	. 56	6. 0	1. 02186	1. 02366	3. 35
1. 1	1. 00251	1. 00428	. 62	6. 1	1. 02226	1. 02407	3. 41
1. 2	1. 00290	1. 00467	. 67	6. 2	1. 02266	1. 02447	3. 46
1. 3	1. 00329	1. 00506	. 73	6. 3	1. 02306	1. 02487	3. 52
1. 4	1. 00368	1. 00545	. 79	6. 4	1. 02346	1. 02527	3. 57
1. 5	1. 00406	1. 00584	. 84	6. 5	1. 02387	1. 02568	3. 63
1. 6	1. 00445	1. 00623	. 90	6. 6	1. 02427	1. 02608	3. 69
1. 7	1. 00484	1. 00662	. 95	6. 7	1. 02467	1. 02648	3. 74
1. 8	1. 00523	1. 00701	1. 01	6. 8	1. 02508	1. 02689	3. 80
1. 9	1. 00562	1. 00740	1. 07	6. 9	1. 02548	1. 02729	3. 85
2. 0	1. 00602	1. 00779	1. 12	7. 0	1. 02588	1. 02770	3. 91
2. 1	1. 00641	1. 00818	1. 18	7. 1	1. 02629	1. 02810	3. 96
2. 2	1. 00680	1. 00858	1. 23	7. 2	1. 02669	1. 02851	4. 02
2. 3	1. 00719	1. 00897	1. 29	7. 3	1. 02710	1. 02892	4. 08
2. 4	1. 00758	1. 00936	1. 34	7. 4	1. 02750	1. 02932	4. 13
2. 5	1. 00797	1. 00976	1. 40	7. 5	1. 02791	1. 02973	4. 19
2. 6	1. 00836	1. 01015	1. 46	7. 6	1. 02832	1. 03013	4. 24
2. 7	1. 00876	1. 01054	1. 51	7. 7	1. 02872	1. 03054	4. 30
2. 8	1. 00915	1. 01093	1. 57	7. 8	1. 02913	1. 03095	4. 35
2. 9	1. 00954	1. 01133	1. 62	7. 9	1. 02954	1. 03136	4. 41
3. 0	1. 00993	1. 01172	1. 68	8. 0	1. 02994	1. 03176	4. 46
3. 1	1. 01033	1. 01211	1. 74	8. 1	1. 03035	1. 03217	4. 52
3. 2	1. 01072	1. 01251	1. 79	8. 2	1. 03076	1. 03258	4. 58
3. 3	1. 01112	1. 01290	1. 85	8. 3	1. 03116	1. 03299	4. 63
3. 4	1. 01151	1. 01330	1. 90	8. 4	1. 03157	1. 03340	4. 69
3. 5	1. 01190	1. 01369	1. 96	8. 5	1. 03198	1. 03381	4. 74
3. 6	1. 01230	1. 01409	2. 02	8. 6	1. 03239	1. 03422	4. 80
3. 7	1. 01269	1. 01448	2. 07	8. 7	1. 03280	1. 03463	4. 85
3. 8	1. 01309	1. 01488	2. 13	8. 8	1. 03321	1. 03504	4. 91
3. 9	1. 01348	1. 01528	2. 18	8. 9	1. 03362	1. 03545	4. 96
4. 0	1. 01388	1. 01567	2. 24	9. 0	1. 03403	1. 03586	5. 02
4. 1	1. 01428	1. 01607	2. 29	9. 1	1. 03444	1. 03627	5. 07
4. 2	1. 01467	1. 01647	2. 35	9. 2	1. 03485	1. 03668	5. 13
4. 3	1. 01507	1. 01687	2. 40	9. 3	1. 03526	1. 03709	5. 19
4. 4	1. 01547	1. 01726	2. 46	9. 4	1. 03567	1. 03750	5. 24
4. 5	1. 01586	1. 01766	2. 52	9. 5	1. 03608	1. 03792	5. 30
4. 6	1. 01626	1. 01806	2. 57	9. 6	1. 03649	1. 03833	5. 35
4. 7	1. 01666	1. 01846	2. 63	9. 7	1. 03691	1. 03874	5. 41
4. 8	1. 01706	1. 01886	2. 68	9. 8	1. 03732	1. 03915	5. 46
4. 9	1. 01746	1. 01926	2. 74	9. 9	1. 03773	1. 03957	5. 52

TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*—Continued

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
10. 0	1. 03814	1. 03998	5. 57	15. 0	1. 05916	1. 06104	8. 34
10. 1	1. 03856	1. 04039	5. 63	15. 1	1. 05959	1. 06147	8. 40
10. 2	1. 03897	1. 04081	5. 68	15. 2	1. 06002	1. 06190	8. 45
10. 3	1. 03938	1. 04122	5. 74	15. 3	1. 06045	1. 06233	8. 51
10. 4	1. 03980	1. 04164	5. 80	15. 4	1. 06088	1. 06276	8. 56
10. 5	1. 04021	1. 04205	5. 85	15. 5	1. 06131	1. 06319	8. 62
10. 6	1. 04063	1. 04247	5. 91	15. 6	1. 06174	1. 06362	8. 67
10. 7	1. 04104	1. 04288	5. 96	15. 7	1. 06217	1. 06405	8. 73
10. 8	1. 04146	1. 04330	6. 02	15. 8	1. 06260	1. 06448	8. 78
10. 9	1. 04187	1. 04371	6. 07	15. 9	1. 06303	1. 06491	8. 84
11. 0	1. 04229	1. 04413	6. 13	16. 0	1. 06346	1. 06534	8. 89
11. 1	1. 04270	1. 04455	6. 18	16. 1	1. 06389	1. 06577	8. 95
11. 2	1. 04312	1. 04497	6. 24	16. 2	1. 06432	1. 06621	9. 00
11. 3	1. 04354	1. 04538	6. 30	16. 3	1. 06476	1. 06664	9. 06
11. 4	1. 04395	1. 04580	6. 35	16. 4	1. 06519	1. 06707	9. 11
11. 5	1. 04437	1. 04622	6. 41	16. 5	1. 06562	1. 06751	9. 17
11. 6	1. 04479	1. 04664	6. 46	16. 6	1. 06605	1. 06794	9. 22
11. 7	1. 04521	1. 04706	6. 52	16. 7	1. 06649	1. 06837	9. 28
11. 8	1. 04562	1. 04747	6. 57	16. 8	1. 06692	1. 06881	9. 33
11. 9	1. 04604	1. 04789	6. 63	16. 9	1. 06736	1. 06924	9. 39
12. 0	1. 04646	1. 04831	6. 68	17. 0	1. 06779	1. 06968	9. 45
12. 1	1. 04688	1. 04873	6. 74	17. 1	1. 06822	1. 07011	9. 50
12. 2	1. 04730	1. 04915	6. 79	17. 2	1. 06866	1. 07055	9. 56
12. 3	1. 04772	1. 04957	6. 85	17. 3	1. 06909	1. 07098	9. 61
12. 4	1. 04814	1. 04999	6. 90	17. 4	1. 06953	1. 07142	9. 67
12. 5	1. 04856	1. 05041	6. 96	17. 5	1. 06996	1. 07186	9. 72
12. 6	1. 04898	1. 05084	7. 02	17. 6	1. 07040	1. 07229	9. 78
12. 7	1. 04940	1. 05126	7. 07	17. 7	1. 07084	1. 07273	9. 83
12. 8	1. 04982	1. 05168	7. 13	17. 8	1. 07127	1. 07317	9. 89
12. 9	1. 05024	1. 05210	7. 18	17. 9	1. 07171	1. 07361	9. 94
13. 0	1. 05066	1. 05252	7. 24	18. 0	1. 07215	1. 07404	10. 00
13. 1	1. 05109	1. 05295	7. 29	18. 1	1. 07258	1. 07448	10. 05
13. 2	1. 05151	1. 05337	7. 35	18. 2	1. 07302	1. 07492	10. 11
13. 3	1. 05193	1. 05379	7. 40	18. 3	1. 07346	1. 07536	10. 16
13. 4	1. 05236	1. 05422	7. 46	18. 4	1. 07390	1. 07580	10. 22
13. 5	1. 05278	1. 05464	7. 51	18. 5	1. 07434	1. 07624	10. 27
13. 6	1. 05320	1. 05506	7. 57	18. 6	1. 07478	1. 07668	10. 33
13. 7	1. 05363	1. 05549	7. 62	18. 7	1. 07522	1. 07712	10. 38
13. 8	1. 05405	1. 05591	7. 68	18. 8	1. 07566	1. 07756	10. 44
13. 9	1. 05448	1. 05634	7. 73	18. 9	1. 07610	1. 07800	10. 49
14. 0	1. 05490	1. 05677	7. 79	19. 0	1. 07654	1. 07844	10. 55
14. 1	1. 05532	1. 05719	7. 84	19. 1	1. 07698	1. 07888	10. 60
14. 2	1. 05575	1. 05762	7. 90	19. 2	1. 07742	1. 07932	10. 66
14. 3	1. 05618	1. 05804	7. 96	19. 3	1. 07786	1. 07977	10. 71
14. 4	1. 05660	1. 05847	8. 01	19. 4	1. 07830	1. 08021	10. 77
14. 5	1. 05703	1. 05890	8. 07	19. 5	1. 07874	1. 08065	10. 82
14. 6	1. 05746	1. 05933	8. 12	19. 6	1. 07919	1. 08110	10. 88
14. 7	1. 05788	1. 05975	8. 18	19. 7	1. 07963	1. 08154	10. 93
14. 8	1. 05831	1. 06018	8. 23	19. 8	1. 08007	1. 08198	10. 99
14. 9	1. 05874	1. 06061	8. 29	19. 9	1. 08052	1. 08243	11. 04

TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*—Continued

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
20. 0	1. 08096	1. 08287	11. 10	25. 0	1. 10356	1. 10551	13. 84
20. 1	1. 08140	1. 08332	11. 15	25. 1	1. 10402	1. 10597	13. 89
20. 2	1. 08185	1. 08376	11. 21	25. 2	1. 10448	1. 10643	13. 95
20. 3	1. 08229	1. 08421	11. 26	25. 3	1. 10494	1. 10689	14. 00
20. 4	1. 08274	1. 08465	11. 32	25. 4	1. 10540	1. 10736	14. 06
20. 5	1. 08318	1. 08510	11. 37	25. 5	1. 10586	1. 10782	14. 11
20. 6	1. 08363	1. 08554	11. 43	25. 6	1. 10632	1. 10828	14. 17
20. 7	1. 08407	1. 08599	11. 48	25. 7	1. 10679	1. 10874	14. 22
20. 8	1. 08452	1. 08644	11. 54	25. 8	1. 10725	1. 10921	14. 28
20. 9	1. 08497	1. 08689	11. 59	25. 9	1. 10771	1. 10967	14. 33
21. 0	1. 08541	1. 08733	11. 65	26. 0	1. 10818	1. 11014	14. 39
21. 1	1. 08586	1. 08778	11. 70	26. 1	1. 10864	1. 11060	14. 44
21. 2	1. 08631	1. 08823	11. 76	26. 2	1. 10910	1. 11106	14. 49
21. 3	1. 08676	1. 08868	11. 81	26. 3	1. 10957	1. 11153	14. 55
21. 4	1. 08720	1. 08913	11. 87	26. 4	1. 11003	1. 11200	14. 60
21. 5	1. 08765	1. 08958	11. 92	26. 5	1. 11050	1. 11246	14. 66
21. 6	1. 08810	1. 09003	11. 98	26. 6	1. 11096	1. 11293	14. 71
21. 7	1. 08855	1. 09048	12. 03	26. 7	1. 11143	1. 11339	14. 77
21. 8	1. 08900	1. 09093	12. 09	26. 8	1. 11190	1. 11386	14. 82
21. 9	1. 08945	1. 09138	12. 14	26. 9	1. 11236	1. 11433	14. 88
22. 0	1. 08990	1. 09183	12. 20	27. 0	1. 11283	1. 11480	14. 93
22. 1	1. 09035	1. 09228	12. 25	27. 1	1. 11330	1. 11526	14. 99
22. 2	1. 09080	1. 09273	12. 31	27. 2	1. 11376	1. 11573	15. 04
22. 3	1. 09125	1. 09318	12. 36	27. 3	1. 11423	1. 11620	15. 09
22. 4	1. 09170	1. 09364	12. 42	27. 4	1. 11470	1. 11667	15. 15
22. 5	1. 09216	1. 09409	12. 47	27. 5	1. 11517	1. 11714	15. 20
22. 6	1. 09261	1. 09454	12. 52	27. 6	1. 11564	1. 11761	15. 26
22. 7	1. 09306	1. 09499	12. 58	27. 7	1. 11610	1. 11808	15. 31
22. 8	1. 09351	1. 09545	12. 63	27. 8	1. 11657	1. 11855	15. 37
22. 9	1. 09397	1. 09590	12. 69	27. 9	1. 11704	1. 11902	15. 42
23. 0	1. 09442	1. 09636	12. 74	28. 0	1. 11751	1. 11949	15. 48
23. 1	1. 09487	1. 09681	12. 80	28. 1	1. 11798	1. 11996	15. 53
23. 2	1, 09533	1. 09727	12. 85	28. 2	1. 11845	1. 12043	15. 59
23. 3	1. 09578	1. 09772	12. 91	28. 3	1. 11892	1. 12090	15. 64
23. 4	1. 09624	1. 09818	12. 96	28. 4	1. 11940	1. 12138	15. 69
23. 5	1. 09669	1. 09863	13. 02	28. 5	1. 11987	1. 12185	15. 75
23. 6	1. 09715	1. 09909	13. 07	28. 6	1. 12034	1. 12232	15. 80
23. 7	1. 09760	1. 09954	13. 13	28. 7	1. 12081	1. 12280	15. 86
23. 8	1. 09806	1. 10000	13. 18	28. 8	1. 12128	1. 12327	15. 91
23. 9	1. 09851	1. 10046	13. 24	28. 9	1. 12176	1. 12374	15. 97
24. 0	1. 09897	1. 10092	13. 29	29. 0	1. 12223	1. 12422	16. 02
24. 1	1. 09943	1. 10137	13. 35	29. 1	1. 12270	1. 12469	16. 08
24. 2	1. 09989	1. 10183	13. 40	29. 2	1. 12318	1. 12517	16. 13
24. 3	1. 10034	1. 10229	13. 46	29. 3	1. 12365	1. 12564	16. 18
24. 4	1. 10080	1. 10275	13. 51	29. 4	1. 12413	1. 12612	16. 24
24. 5	1. 10126	1. 10321	13. 57	29. 5	1. 12460	1. 12659	16. 29
24. 6	1. 10172	1. 10367	13. 62	29. 6	1. 12508	1. 12707	16. 35
24. 7	1. 10218	1. 10413	13. 67	29. 7	1. 12556	1. 12755	16. 40
24. 8	1. 10264	1. 10459	13. 73	29. 8	1. 12603	1. 12802	16. 46
24. 9	1. 10310	1. 10505	13. 78	29. 9	1. 12651	1. 12850	16. 51

TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*—Continued

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
30. 0	1. 12698	1. 12898	16. 57	35. 0	1. 15128	1. 15331	19. 28
30. 1	1. 12746	1. 12946	16. 62	35. 1	1. 15177	1. 15381	19. 33
30. 2	1. 12794	1. 12993	16. 67	35. 2	1. 15226	1. 15430	19. 38
30. 3	1. 12842	1. 13041	16. 73	35. 3	1. 15276	1. 15480	19. 44
30. 4	1. 12890	1. 13089	16. 78	35. 4	1. 15326	1. 15530	19. 49
30. 5	1. 12937	1. 13137	16. 84	35. 5	1. 15375	1. 15579	19. 55
30. 6	1. 12985	1. 13185	16. 89	35. 6	1. 15425	1. 15629	19. 60
30. 7	1. 13033	1. 13233	16. 95	35. 7	1. 15475	1. 15679	19. 65
30. 8	1. 13081	1. 13281	17. 00	35. 8	1. 15524	1. 15729	19. 71
30. 9	1. 13129	1. 13329	17. 05	35. 9	1. 15574	1. 15778	19. 76
31. 0	1. 13177	1. 13378	17. 11	36. 0	1. 15624	1. 15828	19. 81
31. 1	1. 13225	1. 13426	17. 16	36. 1	1. 15674	1. 15878	19. 87
31. 2	1. 13274	1. 13474	17. 22	36. 2	1. 15724	1. 15928	19. 92
31. 3	1. 13322	1. 13522	17. 27	36. 3	1. 15773	1. 15978	19. 98
31. 4	1. 13370	1. 13570	17. 33	36. 4	1. 15823	1. 16028	20. 03
31. 5	1. 13418	1. 13619	17. 38	36. 5	1. 15873	1. 16078	20. 08
31. 6	1. 13466	1. 13667	17. 43	36. 6	1. 15923	1. 16128	20. 14
31. 7	1. 13515	1. 13715	17. 49	36. 7	1. 15973	1. 16178	20. 19
31. 8	1. 13563	1. 13764	17. 54	36. 8	1. 16023	1. 16228	20. 25
31. 9	1. 13611	1. 13812	17. 60	36. 9	1. 16073	1. 16279	20. 30
32. 0	1. 13660	1. 13861	17. 65	37. 0	1. 16124	1. 16329	20. 35
32. 1	1. 13708	1. 13909	17. 70	37. 1	1. 16174	1. 16379	20. 41
32. 2	1. 13756	1. 13958	17. 76	37. 2	1. 16224	1. 16430	20. 46
32. 3	1. 13805	1. 14006	17. 81	37. 3	1. 16274	1. 16480	20. 52
32. 4	1. 13853	1. 14055	17. 87	37. 4	1. 16324	1. 16530	20. 57
32. 5	1. 13902	1. 14103	17. 92	37. 5	1. 16375	1. 16581	20. 62
32. 6	1. 13951	1. 14152	17. 98	37. 6	1. 16425	1. 16631	20. 68
32. 7	1. 13999	1. 14201	18. 03	37. 7	1. 16476	1. 16682	20. 73
32. 8	1. 14048	1. 14250	18. 08	37. 8	1. 16526	1. 16732	20. 78
32. 9	1. 14097	1. 14298	18. 14	37. 9	1. 16576	1. 16783	20. 84
33. 0	1. 14145	1. 14347	18. 19	38. 0	1. 16627	1. 16833	20. 89
33. 1	1. 14194	1. 14396	18. 25	38. 1	1. 16678	1. 16884	20. 94
33. 2	1. 14243	1. 14445	18. 30	38. 2	1. 16728	1. 16934	21. 00
33. 3	1. 14292	1. 14494	18. 36	38. 3	1. 16779	1. 16985	21. 05
33. 4	1. 14340	1. 14543	18. 41	38. 4	1. 16829	1. 17036	21. 11
33. 5	1. 14389	1. 14592	18. 46	38. 5	1. 16880	1. 17087	21. 16
33. 6	1. 14438	1. 14641	18. 52	38. 6	1. 16931	1. 17138	21. 21
33. 7	1. 14487	1. 14690	18. 57	38. 7	1. 16982	1. 17188	21. 27
33. 8	1. 14536	1. 14739	18. 63	38. 8	1. 17032	1. 17239	21. 32
33. 9	1. 14585	1. 14788	18. 68	38. 9	1. 17083	1. 17290	21. 38
34. 0	1. 14634	1. 14837	18. 73	39. 0	1. 17134	1. 17341	21. 43
34. 1	1. 14684	1. 14886	18. 79	39. 1	1. 17185	1. 17392	21. 48
34. 2	1. 14733	1. 14936	18. 84	39. 2	1. 17236	1. 17443	21. 54
34. 3	1. 14782	1. 14985	18. 90	39. 3	1. 17287	1. 17494	21. 59
34. 4	1. 14831	1. 15034	18. 95	39. 4	1. 17338	1. 17545	21. 64
34. 5	1. 14880	1. 15084	19. 00	39. 5	1. 17389	1. 17596	21. 70
34. 6	1. 14930	1. 15133	19. 06	39. 6	1. 17440	1. 17648	21. 75
34. 7	1. 14979	1. 15183	19. 11	39. 7	1. 17491	1. 17699	21. 80
34. 8	1. 15029	1. 15232	19. 17	39. 8	1. 17542	1. 17750	21. 86
34. 9	1. 15078	1. 15282	19. 22	39. 9	1. 17594	1. 17802	21. 91

TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*—Continued

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
40. 0	1. 17645	1. 17853	21. 97	45. 0	1. 20254	1. 20467	24. 63
40. 1	1. 17696	1. 17904	22. 02	45. 1	1. 20307	1. 20520	24. 69
40. 2	1. 17747	1. 17956	22. 07	45. 2	1. 20360	1. 20573	24. 74
40. 3	1. 17799	1. 18007	22. 13	45. 3	1. 20414	1. 20627	24. 79
40. 4	1. 17850	1. 18058	22. 18	45. 4	1. 20467	1. 20680	24. 85
40. 5	1. 17901	1. 18110	22. 23	45. 5	1. 20520	1. 20733	24. 90
40. 6	1. 17953	1. 18162	22. 29	45. 6	1. 20573	1. 20787	24. 95
40. 7	1. 18004	1. 18213	22. 34	45. 7	1. 20627	1. 20840	25. 01
40. 8	1. 18056	1. 18265	22. 39	45. 8	1. 20680	1. 20894	25. 06
40. 9	1. 18108	1. 18316	22. 45	45. 9	1. 20734	1. 20947	25. 11
41. 0	1. 18159	1. 18368	22. 50	46. 0	1. 20787	1. 21001	25. 17
41. 1	1. 18211	1. 18420	22. 55	46. 1	1. 20840	1. 21054	25. 22
41. 2	1. 18262	1. 18472	22. 61	46. 2	1. 20894	1. 21108	25. 27
41. 3	1. 18314	1. 18524	22. 66	46. 3	1. 20948	1. 21162	25. 32
41. 4	1. 18366	1. 18575	22. 72	46. 4	1. 21001	1. 21215	25. 38
41. 5	1. 18418	1. 18627	22. 77	46. 5	1. 21055	1. 21269	25. 43
41. 6	1. 18470	1. 18679	22. 82	46. 6	1. 21109	1. 21323	25. 48
41. 7	1. 18522	1. 18731	22. 88	46. 7	1. 21162	1. 21377	25. 54
41. 8	1. 18573	1. 18783	22. 93	46. 8	1. 21216	1. 21431	25. 59
41. 9	1. 18625	1. 18835	22. 98	46. 9	1. 21270	1. 21484	25. 64
42. 0	1. 18677	1. 18887	23. 04	47. 0	1. 21324	1. 21538	25. 70
42. 1	1. 18729	1. 18939	23. 09	47. 1	1. 21378	1. 21592	25. 75
42. 2	1. 18781	1. 18992	23. 14	47. 2	1. 21432	1. 21646	25. 80
42. 3	1. 18834	1. 19044	23. 20	47. 3	1. 21486	1. 21700	25. 86
42. 4	1. 18886	1. 19096	23. 25	47. 4	1. 21540	1. 21755	25. 91
42. 5	1. 18938	1. 19148	23. 30	47. 5	1. 21594	1. 21809	25. 96
42. 6	1. 18990	1. 19201	23. 36	47. 6	1. 21648	1. 21863	26. 01
42. 7	1. 19042	1. 19253	23. 41	47. 7	1. 21702	1. 21917	26. 07
42. 8	1. 19095	1. 19305	23. 46	47. 8	1. 21756	1. 21971	26. 12
42. 9	1. 19147	1. 19358	23. 52	47. 9	1. 21810	1. 22026	26. 17
43. 0	1. 19199	1. 19410	23. 57	48. 0	1. 21864	1. 22080	26. 23
43. 1	1. 19252	1. 19463	23. 62	48. 1	1. 21918	1. 22134	26. 28
43. 2	1. 19304	1. 19515	23. 68	48. 2	1. 21973	1. 22189	26. 33
43. 3	1. 19356	1. 19568	23. 73	48. 3	1. 22027	1. 22243	26. 38
43. 4	1. 19409	1. 19620	23. 78	48. 4	1. 22082	1. 22298	26. 44
43. 5	1. 19462	1. 19673	23. 84	48. 5	1. 22136	1. 22352	26. 49
43. 6	1. 19514	1. 19726	23. 89	48. 6	1. 22190	1. 22406	26. 54
43. 7	1. 19567	1. 19778	23. 94	48. 7	1. 22245	1. 22461	26. 59
43. 8	1. 19619	1. 19831	24. 00	48. 8	1. 22300	1. 22516	26. 65
43. 9	1. 19672	1. 19884	24. 05	48. 9	1. 22354	1. 22570	26. 70
44. 0	1. 19725	1. 19936	24. 10	49. 0	1. 22409	1. 22625	26. 75
44. 1	1. 19778	1. 19989	24. 16	49. 1	1. 22463	1. 22680	26. 81
44. 2	1. 19830	1. 20042	24. 21	49. 2	1. 22518	1. 22735	26. 86
44. 3	1. 19883	1. 20095	24. 26	49. 3	1. 22573	1. 22789	26. 91
44. 4	1. 19936	1. 20148	24. 32	49. 4	1. 22627	1. 22844	26. 96
44. 5	1. 19989	1. 20201	24. 37	49. 5	1. 22682	1. 22899	27. 02
44. 6	1. 20042	1. 20254	24. 42	49. 6	1. 22737	1. 22954	27. 07
44. 7	1. 20095	1. 20307	24. 48	49. 7	1. 22792	1. 23009	27. 12
44. 8	1. 20148	1. 20360	24. 53	49. 8	1. 22847	1. 23064	27. 18
44. 9	1. 20201	1. 20414	24. 58	49. 9	1. 22902	1. 23119	27. 23

TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*—Continued

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
50. 0	1. 22957	1. 23174	27. 28	55. 0	1. 25754	1. 25976	29. 90
50. 1	1. 23012	1. 23229	27. 33	55. 1	1. 25810	1. 26033	29. 95
50. 2	1. 23067	1. 23284	27. 39	55. 2	1. 25867	1. 26090	30. 00
50. 3	1. 23122	1. 23340	27. 44	55. 3	1. 25924	1. 26147	30. 06
50. 4	1. 23177	1. 23395	27. 49	55. 4	1. 25982	1. 26204	30. 11
50. 5	1. 23232	1. 23450	27. 54	55. 5	1. 26039	1. 26261	30. 16
50. 6	1. 23287	1. 23506	27. 60	55. 6	1. 26096	1. 26319	30. 21
50. 7	1. 23343	1. 23561	27. 65	55. 7	1. 26153	1. 26376	30. 26
50. 8	1. 23398	1. 23616	27. 70	55. 8	1. 26210	1. 26433	30. 32
50. 9	1. 23453	1. 23672	27. 75	55. 9	1. 26267	1. 26490	30. 37
51. 0	1. 23508	1. 23727	27. 81	56. 0	1. 26324	1. 26548	30. 42
51. 1	1. 23564	1. 23782	27. 86	56. 1	1. 26382	1. 26605	30. 47
51. 2	1. 23619	1. 23838	27. 91	56. 2	1. 26439	1. 26663	30. 52
51. 3	1. 23675	1. 23894	27. 96	56. 3	1. 26496	1. 26720	30. 57
51. 4	1. 23730	1. 23949	28. 02	56. 4	1. 26554	1. 26778	30. 63
51. 5	1. 23786	1. 24005	28. 07	56. 5	1. 26611	1. 26835	30. 68
51. 6	1. 23841	1. 24060	28. 12	56. 6	1. 26669	1. 26893	30. 73
51. 7	1. 23897	1. 24116	28. 17	56. 7	1. 26726	1. 26950	30. 78
51. 8	1. 23953	1, 24172	28. 23	56. 8	1. 26784	1. 27008	30. 83
51. 9	1. 24008	1. 24228	28. 28	56. 9	1. 26841	1. 27066	30. 89
52. 0	1. 24064	1. 24284	28. 33	57. 0	1. 26899	1. 27123	30. 94
52. 1	1. 24120	1. 24339	28. 38	57. 1	1. 26956	1. 27181	30. 99
52. 2	1. 24176	1. 24395	28. 44	57. 2	1. 27014	1. 27239	31. 04
52. 3	1. 24232	1. 24451	28. 49	57. 3	1. 27072	1. 27297	31. 09
52. 4	1. 24287	1. 34507	28. 54	57. 4	1. 27130	1. 27355	31. 15
52. 5	1. 24343	1. 24563	28. 59	57. 5	1. 27188	1. 27413	31. 20
52. 6	1. 24399	1. 24619	28. 65	57. 6	1. 27246	1. 27471	31. 25
52. 7	1. 24455	1. 24675	28. 70	57. 7	1. 27304	1. 27529	31. 30
52. 8	1. 24511	1. 24731	28. 75	57. 8	1. 27361	1. 27587	31. 35
52. 9	1. 24567	1. 24788	28. 80	57. 9	1. 27419	1. 27645	31. 40
53. 0	1. 24623	1. 24844	28. 86	58. 0	1. 27477	1. 27703	31. 46
53. 1	1. 24680	1. 24900	28. 91	58. 1	1. 27535	1. 27761	31. 51
53. 2	1. 24736	1. 24956	28. 96	58. 2	1. 27594	1. 27819	31. 56
53. 3	1. 24792	1. 25013	29. 01	58. 3	1. 27652	1. 27878	31. 61
53. 4	1. 24848	1. 25069	29. 06	58. 4	1. 27710	1. 27936	31. 66
53. 5	1. 24905	1. 25126	29. 12	58. 5	1. 27768	1. 27994	31. 71
53. 6	1. 24961	1. 25182	29. 17	58. 6	1. 27826	1. 28052	31. 76
53. 7	1. 25017	1. 25238	29. 22	58. 7	1. 27884	1. 28111	31. 82
53. 8	1. 25074	1. 25295	29. 27	58. 8	1. 27943	1. 28169	31. 87
53. 9	1. 25130	1. 25351	29. 32	58. 9	1. 28001	1. 28228	31. 92
54. 0	1. 25187	1. 25408	29. 38	59. 0	1. 28060	1. 28286	31. 97
54. 1	1. 25243	1. 25465	29. 43	59. 1	1. 28118	1. 28345	32. 02
54. 2	1. 25300	1. 25521	29. 48	59. 2	1. 28176	1. 28404	32. 07
54. 3	1. 25356	1. 25578	29. 53	59. 3	1. 28235	1. 28462	32. 13
54. 4	1. 25413	1. 25635	29. 59	59. 4	1. 28294	1. 28520	32. 18
54. 5	1. 25470	1. 25692	29. 64	59. 5	1. 28352	1. 28579	32. 23
54. 6	1. 25526	1. 25748	29. 69	59. 6	1. 28411	1. 28638	32. 28
54. 7	1. 25583	1. 25805	29. 74	59. 7	1. 28469	1. 28697	32. 33
54. 8	1. 25640	1. 25862	29. 80	59. 8	1. 28528	1. 28755	32. 38
54. 9	1. 25697	1. 25919	29. 85	59. 9	1. 28587	1. 28814	32. 43

TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*—Continued

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
60. 0	1. 28646	1. 28873	32. 49	65. 0	1. 31633	1. 31866	35. 04
60. 1	1. 28704	1. 28932	32. 54	65. 1	1. 31694	1. 31927	35. 09
60. 2	1. 28763	1. 28991	32. 59	65. 2	1. 31755	1. 31988	35. 14
60. 3	1. 28822	1. 29050	32. 64	65. 3	1. 31816	1. 32049	35. 19
60. 4	1. 28881	1. 29109	32. 69	65. 4	1. 31877	1. 32110	35. 24
60. 5	1. 28940	1. 29168	32. 74	65. 5	1. 31937	1. 32171	35. 29
60. 6	1. 28999	1. 29227	32. 79	65. 6	1. 31998	1. 32232	35. 34
60. 7	1. 29058	1. 29286	32. 85	65. 7	1. 32059	1. 32293	35. 39
60. 8	1. 29117	1. 29346	32. 90	65. 8	1. 32120	1. 32354	35. 45
60. 9	1. 29176	1. 29405	32. 95	65. 9	1. 32181	1. 32415	35. 50
61. 0	1. 29235	1. 29464	33. 00	66. 0	1. 32242	1. 32476	35. 55
61. 1	1. 29295	1. 29523	33. 05	66. 1	1. 32304	1. 32538	35. 60
61. 2	1. 29354	1. 29583	33. 10	66. 2	1. 32365	1. 32599	35. 65
61. 3	1. 29413	1. 29642	33. 15	66. 3	1. 32426	1. 32660	35. 70
61. 4	1. 29472	1. 29701	33. 20	66. 4	1. 32487	1. 32722	35. 75
61. 5	1. 29532	1. 29761	33. 26	66. 5	1. 32548	1. 32783	35. 80
61. 6	1. 29591	1. 29820	33. 31	66. 6	1. 32610	1. 32844	35. 85
61. 7	1. 29651	1. 29880	33. 36	66. 7	1. 32671	1. 32906	35. 90
61. 8	1. 29710	1. 29940	33. 41	66. 8	1. 32732	1. 32967	35. 95
61. 9	1. 29770	1. 29999	33. 46	66. 9	1. 32794	1. 33029	36. 00
62. 0	1. 29829	1. 30059	33. 51	67. 0	1. 32855	1. 33090	36. 05
62. 1	1. 29889	1. 30118	33. 56	67. 1	1. 32917	1. 33152	36. 10
62. 2	1. 29948	1. 30178	33. 61	67. 2	1. 32978	1. 33214	36. 15
62. 3	1. 30008	1. 30238	33. 67	67. 3	1. 33040	1. 33275	36. 20
62. 4	1. 30068	1, 30298	33. 72	67. 4	1. 33102	1. 33337	36. 25
62. 5	1. 30127	1. 30358	33. 77	67. 5	1. 33163	1. 33399	36. 30
62. 6	1. 30187	1. 30418	33. 82	67. 6	1. 33225	1. 33460	36. 35
62. 7	1. 30247	1. 30477	33. 87	67. 7	1. 33287	1. 33523	36. 40
62. 8	1. 30307	1. 30537	33. 92	67. 8	1. 33348	1. 33584	36. 45
62. 9	1. 30367	1. 30597	33. 97	67. 9	1. 33410	1. 33646	36. 50
63. 0	1. 30427	1. 30657	34. 02	68. 0	1. 33472	1. 33708	36. 55
63. 1	1. 30487	1. 30718	34. 07	68. 1	1. 33534	1. 33770	36. 61
63. 2	1. 30547	1. 30778	34. 12	68. 2	1. 33596	1. 33832	36. 66
63. 3	1. 30607	1. 30838	34. 18	68. 3	1. 33658	1. 33894	36. 71
63. 4	1. 30667	1. 30898	34. 23	68. 4	1. 33720	1. 33957	36. 76
63. 5	1. 30727	1. 30958	34. 28	68. 5	1. 33782	1. 34019	36. 81
63. 6	1. 30787	1. 31019	34. 33	68. 6	1. 33844	1. 34081	36. 86
63. 7	1. 30848	1. 31079	34. 38	68. 7	1. 33906	1. 34143	36. 91
63. 8	1. 30908	1. 31139	34. 43	68. 8	1. 33968	1. 34205	36. 96
63. 9	1. 30968	1. 31200	34. 48	68. 9	1. 34031	1. 34268	37. 01
64. 0	1. 31028	1. 31260	34. 53	69. 0	1. 34093	1. 34330	37. 06
64. 1	1. 31088	1 .31320	34. 58	69. 1	1. 34155	1. 34392	37. 11
64. 2	1. 31149	1. 31381	34. 63	69. 2	1. 34217	1. 34455	37. 16
64. 3	1, 31209	1. 31441	34. 68	69. 3	1. 34280	1. 34517	37. 21
64. 4	1. 31270	1. 31502	34. 74	69. 4	1. 34342	1. 34580	37. 26
64. 5	1. 31330	1. 31563	34. 79	69. 5	1. 34405	1. 34642	37. 31
64. 6	1. 31391	1. 31623	34. 84	69. 6	1. 34467	1. 34705	37. 36
64. 7	1. 31452	1. 31684	34. 89	69. 7	1. 34530	1. 34768	37. 41
64. 8	1. 31512	1. 31745	34. 94	69. 8	1. 34592	1. 34830	37. 46
64. 9	1. 31573	1. 31806	34. 99	69. 9	1. 34655	1. 34893	37. 51

TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*—Continued

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
70. 0	1. 34717	1. 34956	37. 56	75. 0	1. 37897	1. 38141	40. 03
70. 1	1. 34780	1. 35019	37. 61	75. 1	1. 37962	1. 38206	40. 08
70. 2	1. 34843	1. 35081	37. 66	75. 2	1. 38026	1. 38270	40. 13
70. 3	1. 34906	1. 35144	37. 71	75. 3	1. 38091	1. 38335	40. 18
70. 4	1. 34968	1. 35207	37. 76	75. 4	1. 38156	1. 38400	40. 23
70. 5	1. 35031	1. 35270	37. 81	75. 5	1. 38220	1. 38465	40. 28
70. 6	1. 35094	1. 35333	37. 86	75. 6	1. 38285	1. 38530	40. 33
70. 7	1. 35157	1. 35396	37. 91	75. 7	1. 38350	1. 38595	40. 38
70. 8	1. 35220	1. 35459	37. 96	75. 8	1. 38415	1. 38660	40. 43
70. 9	1. 35283	1. 35522	38. 01	75. 9	1. 38480	1. 38725	40. 48
71. 0	1. 35346	1. 35585	38. 06	76. 0	1. 38545	1. 38790	40. 53
71. 1	1. 35409	1. 35648	38. 11	76. 1	1. 38610	1. 38855	40. 57
71. 2	1. 35472	1. 35711	38. 16	76. 2	1. 38675	1. 38920	40. 62
71. 3	1. 35535	1. 35775	38. 21	76. 3	1. 38740	1. 38985	40. 67
71. 4	1. 35598	1. 35838	38. 26	76. 4	1. 38805	1. 39050	40. 72
71. 5	1. 35661	1. 35901	38. 30	76. 5	1. 38870	1. 39115	40. 77
71. 6	1. 35724	1. 35964	38. 35	76. 6	1. 38935	1. 39180	40. 82
71. 7	1. 35788	1. 36028	38. 40	76. 7	1. 39000	1. 39246	40. 87
71. 8	1. 35851	1. 36091	38. 45	76. 8	1. 39065	1. 39311	40. 92
71. 9	1. 35914	1. 36155	38. 50	76. 9	1. 39130	1. 39376	40. 97
72. 0	1. 35978	1. 36218	38. 55	77. 0	1. 39196	1. 39442	41. 01
72. 1	1. 36041	1. 36282	38. 60	77. 1	1. 39261	1. 39507	41. 06
72. 2	1. 36105	1. 36346	38. 65	77. 2	1. 39326	1. 39573	41. 11
72. 3	1. 36168	1. 36409	38. 70	77. 3	1. 39392	1. 39638	41. 16
72. 4	1. 36232	1. 36473	38. 75	77. 4	1. 39457	1. 39704	41. 21
72. 5	1. 36295	1. 36536	38. 80	77. 5	1. 39523	1. 39769	41. 26
72. 6	1. 36359	1. 36600	38. 85	77. 6	1. 39588	1. 39835	41. 31
72. 7	1. 36423	1. 36664	38. 90	77. 7	1. 39654	1. 39901	41. 36
72. 8	1. 36486	1. 36728	38. 95	77. 8	1. 39719	1. 39966	41. 40
72. 9	1. 36550	1. 36792	39. 00	77. 9	1. 39785	1. 40032	41. 45
73. 0	1. 36614	1. 36856	39. 05	78. 0	1. 39850	1. 40098	41. 50
73. 1	1. 36678	1. 36919	39. 10	78. 1	1. 39916	1. 40164	41. 55
73. 2	1. 36742	1. 36983	39. 15	78. 2	1. 39982	1. 40230	41. 60
73. 3	1. 36805	1. 37047	39. 20	78. 3	1. 40048	1. 40295	41. 65
73. 4	1. 36869	1. 37111	39. 25	78. 4	1. 40113	1. 40361	41. 70
73. 5	1. 36933	1. 37176	39. 30	78. 5	1. 40179	1. 40427	41. 74
73. 6	1. 36997	1. 37240	39. 35	78. 6	1. 40245	1. 40493	41. 79
73. 7	1. 37061	1. 37304	39. 39	78. 7	1. 40311	1. 40559	41. 84
73. 8	1. 37125	1. 37368	39. 44	78. 8	1. 40377	1. 40625	41. 89
73. 9	1. 37189	1. 37432	39. 49	78. 9	1. 40443	1. 40691	41. 94
74. 0	1. 37254	1. 37496	39. 54	79. 0	1. 40509	1. 40758	41. 99
74. 1	1. 37318	1. 37561	39. 59	79. 1	1. 40575	1. 40824	42. 03
74. 2	1. 37382	1. 37625	39. 64	79. 2	1. 40641	1. 40890	42. 08
74. 3	1. 37446	1. 37689	39. 69	79. 3	1. 40707	1. 40956	42. 13
74. 4	1. 37510	1. 37754	39. 74	79. 4	1. 40774	1. 41023	42. 18
74. 5	1. 37575	1. 37818	39. 79	79. 5	1. 40840	1. 41089	42. 23
74. 6	1. 37639	1. 37883	39. 84	79. 6	1. 40906	1. 41155	42. 28
74. 7	1. 37704	1. 37947	39. 89	79. 7	1. 40972	1. 41222	42. 32
74. 8	1. 37768	1. 38012	39. 94	79. 8	1. 41039	1. 41288	42. 37
74. 9	1. 37833	1. 38076	39. 99	79. 9	1. 41105	1. 41355	42. 42

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TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*—Continued

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
80. 0	1. 41172	1. 41421	42. 47	85. 0	1. 44539	1. 44794	44. 86
80. 1	1. 41238	1. 41488	42. 52	85. 1	1. 44607	1. 44863	44. 91
80. 2	1. 41304	1. 41554	42. 57	85. 2	1. 44675	1. 44931	44. 95
80. 3	1. 41371	1. 41621	42. 61	85. 3	1. 44744	1. 45000	45. 00
80. 4	1. 41437	1. 41688	42. 66	85. 4	1. 44812	1. 45068	45. 05
80. 5	1. 41504	1. 41754	42. 71	85. 5	1. 44881	1. 45137	45. 09
80. 6	1. 41571	1. 41821	42. 76	85. 6	1. 44949	1. 45205	45. 14
80. 7	1. 41637	1. 41888	42. 81	85. 7	1. 45018	1. 45274	45. 19
80. 8	1. 41704	1. 41955	42. 85	85. 8	1. 45086	1. 45343	45. 24
80. 9	1. 41771	1. 42022	42. 90	85. 9	1. 45154	1. 45411	45. 28
81. 0	1. 41837	1. 42088	42. 95	86. 0	1. 45223	1. 45480	45. 33
81. 1	4. 41904	1. 42155	43. 00	86. 1	1. 45292	1. 45549	45. 38
81. 2	1. 41971	1. 42222	43. 05	86. 2	1. 45360	1. 45618	45. 42
81. 3	1. 42038	1. 42289	43. 10	86. 3	1. 45429	1. 45686	45. 47
81. 4	1. 42105	1. 42356	43. 14	86. 4	1. 45498	1. 45755	45. 52
81. 5	1. 42172	1. 42423	43. 19	86. 5	1. 45567	1. 45824	45. 57
81. 6	1. 42239	1. 42490	43. 24	86. 6	1. 45636	1. 45893	45. 61
81. 7	1. 42306	1. 42558	43. 29	86. 7	1. 45704	1. 45962	45. 66
81. 8	1. 42373	1. 42625	43. 33	86. 8	1. 45773	1. 46031	45. 71
81. 9	1. 42440	1. 42692	43. 38	86. 9	1. 45842	1. 46100	45. 75
82. 0	1. 42507	1. 42759	43. 43	87. 0	1. 45911	1. 46170	45. 80
82. 1	1. 42574	1. 42827	43. 48	87. 1	1. 45980	1. 46239	45. 85
82. 2	1. 42642	1. 42894	43. 53	87. 2	1. 46050	1. 46308	45. 89
82. 3	1. 42709	1. 42961	43. 57	87. 3	1. 46119	1. 46377	45. 94
82. 4	1. 42776	1. 43029	43. 62	87. 4	1. 46188	1. 46446	45. 99
82. 5	1. 42844	1. 43096	43. 67	87. 5	1. 46257	1. 46516	46. 03
82. 6	1. 42911	1. 43164	43. 72	87. 6	1. 46326	1. 46585	46. 08
82. 7	1. 42978	1. 43231	43. 77	87. 7	1. 46395	1. 46654	46. 13
82. 8	1. 43046	1. 43298	43. 81	87. 8	1. 46464	1. 46724	46. 17
82. 9	1. 43113	1. 43366	43. 86	87. 9	1. 46534	1. 46793	46. 22
83. 0	1. 43181	1. 43434	43. 91	88. 0	1. 46603	1. 46862	46. 27
83. 1	1. 43248	1. 43502	43. 96	88. 1	1. 46673	1. 46932	46. 31
83. 2	1. 43316	1. 43569	44. 00	88. 2	1. 46742	1. 47002	46. 36
83. 3	1. 43384	1. 43637	44. 05	88. 3	1. 46812	1. 47071	46. 41
83. 4	1. 43451	1. 43705	44. 10	88. 4	1. 46881	1. 47141	46. 45
83. 5	1. 43519	1. 43773	44. 15	88. 5	1. 46950	1. 47210	46. 50
83. 6	1. 43587	1. 43841	44. 19	88. 6	1. 47020	1. 47280	46. 55
83. 7	1. 43654	1. 43908	44. 24	88. 7	1. 47090	1. 47350	46. 59
83. 8	1. 43722	1. 43976	44. 29	88. 8	1. 47159	1. 47420	46. 64
83. 9	1. 43790	1. 44044	44. 34	88. 9	1. 47229	1. 47489	46. 69
84. 0	1. 43858	1. 44112	44. 38	89. 0	1. 47299	1. 47559	46. 73
84. 1	1. 43926	1. 44180	44. 43	89. 1	1. 47368	1. 47629	46. 78
84. 2	1. 43994	1. 44249	44. 48	89. 2	1. 47438	1. 47699	46. 83
84. 3	1. 44062	1. 44317	44. 53	89. 3	1. 47508	1. 47769	46. 87
84. 4	1. 44130	1. 44385	44. 57	89. 4	1. 47578	1. 47839	46. 92
84. 5	1. 44198	1. 44453	44. 62	89. 5	1. 47648	1. 47909	46. 97
84. 6	1. 44266	1. 44521	44. 67	89. 6	1. 47718	1. 47979	47. 01
84. 7	1. 44334	1. 44590	44. 72	89. 7	1. 47788	1. 48049	47. 06
84. 8	1. 44402	1. 44658	44. 76	89. 8	1. 47858	1. 48119	47. 11
84. 9	1. 44470	1. 44726	44. 81	89. 9	1. 47928	1. 48189	47. 15

TABLE 109.—*Degrees Brix, specific gravity, and degrees Baumé of sugar solutions*—Continued

Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)	Degrees Brix or percentage of sucrose by weight	Specific gravity at 20°/4° C	Specific gravity at 20°/20° C	Degrees Baumé (modulus 145)
90. 0	1. 47998	1. 48259	47. 20	95. 0	1. 51546	1. 51814	49. 49
90. 1	1. 48068	1. 48330	47. 24	95. 1	1. 51617	1. 51886	49. 53
90. 2	1. 48138	1. 48400	47. 29	95. 2	1. 51689	1. 51958	49. 58
90. 3	1. 48208	1. 48470	47. 34	95. 3	1. 51761	1. 52030	49. 62
90. 4	1. 48278	1. 48540	47. 38	95. 4	1. 51833	1. 52102	49. 67
90. 5	1. 48348	1. 48611	47. 43	95. 5	1. 51905	1. 52174	49. 71
90. 6	1. 48419	1. 48681	47. 48	95. 6	1. 51977	1. 52246	49. 76
90. 7	1. 48489	1. 48752	47. 52	95. 7	1. 52049	1. 52318	49. 80
90. 8	1. 48559	1. 48822	47. 57	95. 8	1. 52121	1. 52390	49. 85
90. 9	1. 48630	1. 48893	47. 61	95. 9	1. 52193	1. 52463	49. 90
91. 0	1. 48700	1. 48963	47. 66	96. 0	1. 52266	1. 52535	49. 94
91. 1	1. 48771	1. 49034	47. 71	96. 1	1. 52338	1. 52607	49. 98
91. 2	1. 48841	1. 49104	47. 75	96. 2	1. 52410	1. 52680	50. 03
91. 3	1. 48912	1. 49175	47. 80	96. 3	1. 52482	1. 52752	50. 08
91. 4	1. 48982	1. 49246	47. 84	96. 4	1. 52555	1. 52824	50. 12
91. 5	1. 49053	1. 49316	47. 89	96. 5	1. 52627	1. 52897	50. 16
91. 6	1. 49123	1. 49387	47. 94	96. 6	1. 52699	1. 52969	50. 21
91. 7	1. 49194	1. 49458	47. 98	96. 7	1. 52772	1. 53042	50. 25
91. 8	1. 49265	1. 49529	48. 03	96. 8	1. 52844	1. 53114	50. 30
91. 9	1. 49336	1. 49600	48. 08	96. 9	1. 52917	1. 53187	50. 34
92. 0	1. 49406	1. 49671	48. 12	97. 0	1. 52989	1. 53260	50. 39
92. 1	1. 49477	1. 49741	48. 17	97. 1	1. 53062	1. 53332	50. 43
92. 2	1. 49548	1. 49812	48. 21	97. 2	1. 53134	1. 53405	50. 48
92. 3	1. 49619	1. 49883	48. 26	97. 3	1. 53207	1. 53478	50. 52
92. 4	1. 49690	1. 49954	48. 30	97. 4	1. 53279	1. 53551	50. 57
92. 5	1. 49761	1. 50026	48. 35	97. 5	1. 53352	1. 53623	50. 61
92. 6	1. 49832	1. 50097	48. 40	97. 6	1. 53425	1. 53696	50. 66
92. 7	1. 49903	1. 50168	48. 44	97. 7	1. 53498	1. 53769	50. 70
92. 8	1. 49974	1. 50239	48. 49	97. 8	1. 53570	1. 53842	50. 75
92. 9	1. 50045	1. 50310	48. 53	97. 9	1. 53643	1. 53915	50. 79
93. 0	1. 50116	1. 50381	48. 58	98. 0	1. 53716	1. 53988	50. 84
93. 1	1. 50187	1. 50453	48. 62	98. 1	1. 53789	1. 54061	50. 88
93. 2	1. 50258	1. 50524	48. 67	98. 2	1. 53862	1. 54134	50. 93
93. 3	1. 50329	1. 50595	48. 72	98. 3	1. 53935	1. 54207	50. 97
93. 4	1. 50401	1. 50667	48. 76	98. 4	1. 54008	1. 54280	51. 02
93. 5	1. 50472	1. 50738	48. 81	98. 5	1. 54081	1. 54353	51. 06
93. 6	1. 50543	1. 50810	48. 85	98. 6	1. 54154	1. 54426	51. 10
93. 7	1. 50615	1. 50881	48. 90	98. 7	1. 54227	1. 54499	51. 15
93. 8	1. 50686	1. 50952	48. 94	98. 8	1. 54300	1. 54573	51. 19
93. 9	1. 50757	1. 51024	48. 99	98. 9	1. 54373	1. 54646	51. 24
94. 0	1. 50829	1. 51096	49. 03	99. 0	1. 54446	1. 54719	51. 28
94. 1	1. 50900	1. 51167	49. 08	99. 1	1. 54519	1. 54793	51. 33
94. 2	1. 50972	1. 51239	49. 12	99. 2	1. 54593	1. 54866	51. 37
94. 3	1. 51044	1. 51311	49. 17	99. 3	1. 54666	1. 54939	51. 42
94. 4	1. 51115	1. 51382	49. 22	99. 4	1. 54739	1. 55013	51. 46
94. 5	1. 51187	1. 51454	49. 26	99. 5	1. 54813	1. 55087	51. 50
94. 6	1. 51258	1. 51526	49. 31	99. 6	1. 54886	1. 55160	51. 55
94. 7	1. 51330	1. 51598	49. 35	99. 7	1. 54960	1. 55234	51. 59
94. 8	1. 51402	1. 51670	49. 40	99. 8	1. 55033	1. 55307	51. 64
94. 9	1. 51474	1. 51742	49. 44	99. 9	1. 55106	1. 55381	51. 68
				100. 0	1. 55180	1. 55454	51. 73

TABLE 110.—*Temperature corrections to readings of Brix hydrometers (standard at 20° C)*

[This table is calculated using the data on thermal expansion of sugar solutions by Plato,[1] assuming the instrument to be of Jena 16^{III} glass. The table should be used with caution and only for approximate results when the temperature differs much from the standard temperature or from the temperature of the surrounding air]

This table also may be used with instruments that are standard at 17.5° C, as follows: Find the correction for reducing to 20° C in the usual way, and to this add the correction at 17.5° C with the sign changed; i. e., regarded as positive.

For example, if the instrument reads 20.00 percent at 24° C, the correction to 17.5° C is +0.26+0.15=0.41, and the true percentage of sugar is 20.41. If it reads 20.00 percent at 18° C, the correction to 17.5° C is −0.12+0.15=+0.03, and the true percentage of sugar is 20.03. If it reads 20.00 at 15° C, the correction is −0.28+0.15=−0.13, and the true percentage of sugar is 19.87.

Temperature	Observed percentage of sugar													
	0	5	10	15	20	25	30	35	40	45	50	55	60	70
	Subtract from observed percentage													
°C														
0	0.30	0.49	0.65	0.77	0.89	0.99	1.08	1.16	1.24	1.31	1.37	1.41	1.44	1.49
5	.36	.47	.56	.65	.73	.80	.86	.91	.97	1.01	1.05	1.08	1.10	1.14
10	.32	.38	.43	.48	.52	.57	.60	.64	.67	.70	.72	.74	.75	.77
11	.31	.35	.40	.44	.48	.51	.55	.58	.60	.63	.65	.66	.68	.70
12	.29	.32	.36	.40	.43	.46	.50	.52	.54	.56	.58	.59	.60	.62
13	.26	.29	.32	.35	.38	.41	.44	.46	.48	.49	.51	.52	.53	.55
14	.24	.26	.29	.31	.34	.36	.38	.40	.41	.42	.44	.45	.46	.47
15	.20	.22	.24	.26	.28	.30	.32	.33	.34	.36	.36	.37	.38	.39
16	.17	.18	.20	.22	.23	.25	.26	.27	.28	.28	.29	.30	.31	.32
17	.13	.14	.15	.16	.18	.19	.20	.20	21	.21	.22	.23	.23	.24
17.5	.11	.12	.12	.14	.15	.16	.16	.17	.17	.18	.18	.19	.19	.20
18	.09	.10	.10	.11	.12	.13	.13	.14	.14	.14	.15	.15	.15	.16
19	.05	.05	.05	.06	.06	.06	.07	.07	.07	.07	.08	.08	.08	.08
	Add to observed percentage													
21	0.04	0.05	0.06	0.06	0.06	0.07	0.07	0.07	0.07	0.08	0.08	0.08	0.08	0.09
22	.10	.10	.11	.12	.12	.13	.14	.14	.15	.15	.16	.16	.16	.16
23	.16	.16	.17	.17	.19	.20	.21	.21	.22	.23	.24	.24	.24	.24
24	.21	.22	.23	.24	.26	.27	.28	.29	.30	.31	.32	.32	.32	.32
25	.27	.28	.30	.31	.32	.34	.35	.36	.38	.38	.39	.39	.40	.39
26	.33	.34	.36	.37	.40	.40	.42	.44	.46	.47	.47	.48	.48	.48
27	.40	.41	.42	.44	.46	.48	.50	.52	.54	.54	.55	.56	.56	.56
28	.46	.47	.49	.51	.54	.56	.58	.60	61	.62	.63	.64	.64	.64
29	.54	.55	.56	.59	.61	.63	.66	.68	.70	.70	.71	.72	.72	.72
30	.61	.62	.63	.66	.68	.71	.73	.76	.78	.78	.79	.80	.80	.81
35	.99	1.01	1.02	1.06	1.10	1.13	1.16	1.18	1.20	1.21	1.22	1.22	1.23	1.22
40	1.42	1.45	1.47	1.51	1.54	1.57	1.60	1.62	1.64	1.65	1.65	1.65	1.66	1.65
45	1.91	1.94	1.96	2.00	2.03	2.05	2.07	2.09	2.10	2.10	2.10	2.10	2.10	2.08
50	2.46	2.48	2.50	2.53	2.56	2.57	2.58	2.59	2.59	2.58	2.58	2.57	2.56	2.52
55	3.05	3.07	3.09	3.12	3.12	3.12	3.12	3.11	3.10	3.08	3.07	3.05	3.03	2.97
60	3.69	3.72	3.73	3.73	3.72	3.70	3.67	3.65	3.62	3.60	3.57	3.54	3.50	3.43
65	4.4	4.4	4.4	4.4	4.4	4.4	4.3	4.2	4.2	4.1	4.1	4.0	4.0	3.9
70	5.1	5.1	5.1	5.0	5.0	5.0	4.9	4.8	4.8	4.7	4.7	4.6	4.6	4.4
75	6.1	6.0	6.0	5.9	5.8	5.8	5.7	5.6	5.5	5.4	5.4	5.3	5.2	5.0
80	7.1	7.0	7.0	6.9	6.8	6.7	6.6	6.4	6.3	6.2	6.1	6.0	5.9	5.6

[1] Wiss. Abh. Kaiserlichen Normal-Eichungs-Kommission 2, 140 (1900).

TABLE 111.—*Temperature corrections to readings of Baumé hydrometers, National Bureau of Standards Baumé scale for sugar solutions (standard at 20° C)*

[This table is based on the values of the thermal expansion of sugar solutions by Plato, assuming the instrument to be of Jena 16[III] glass. The table should be used with caution and only for approximate results when the temperature differs much from the standard or from the temperature of the surrounding air]

Temperature	Observed degrees Baumé								
	0	5	10	15	20	25	30	35	40
	Subtract from observed degrees Baumé								
°C									
0	0.17	0.34	0.47	0.57	0.65	0.72	0.77	0.79	0.81
5	.21	.30	.39	.45	.51	.55	.59	.60	.61
10	.18	.23	.28	.32	.36	.38	.40	.41	.42
11	.18	.22	.26	.29	.32	.34	.36	.37	.38
12	.17	.20	.23	.26	.29	.31	.32	.33	.34
13	.15	.18	.20	.23	.25	.27	.28	.29	.29
14	.14	.16	.18	.20	.22	.23	.24	.25	.25
15	.11	.13	.15	.17	.18	.20	.20	.21	.21
16	.10	.11	.13	.14	.15	.15	.16	.17	.17
17	.07	.08	.10	.11	.11	.11	.13	.13	.13
18	.05	.06	.07	.07	.08	.08	.08	.08	.09
19	.03	.03	.03	.03	.04	.04	.04	.04	.05
	Add to observed degrees Baumé								
21	0.02	0.03	0.03	0.04	0.04	0.04	0.04	0.05	0.05
22	.06	.06	.07	.07	.08	.08	.08	09	.09
23	.09	.09	.10	.11	.12	.13	.13	.13	.13
24	.12	.13	.14	.15	.16	.17	.17	.17	.17
25	.15	.17	.18	.19	.20	.21	.21	.21	.21
26	.19	.20	.22	.22	.24	.26	.26	.26	.26
27	.23	.23	.25	.27	.29	.30	.30	.30	.30
28	.26	.27	.29	.31	.33	.34	.35	.35	.34
29	.31	.31	.34	.35	.37	.38	.39	.39	.38
30	.35	.35	.38	.39	.42	.43	.44	.43	.43
35	.56	.57	.60	.63	.65	.66	.66	.66	.65
40	.81	.82	.85	.87	.89	.90	.90	.89	.88
45	1.09	1.09	1.12	1.14	1.15	1.15	1.14	1.13	1.11
50	1.40	1.39	1.42	1.42	1.43	1.41	1.40	1.37	1.33
55	1.74	1.72	1.73	1.73	1.71	1.69	1.66	1.62	1.57
60	2.10	2.08	2.06	2.05	2.00	1.97	1.92	1.87	1.82
65	2.5	2.5	2.4	2.4	2.3	2.2	2.2	2.1	2.1
70	2.9	2.8	2.8	2.8	2.6	2.6	2.5	2.4	2.3
75	3.5	3.3	3.2	3.2	3.1	3.0	2.9	2.7	2.6
80	4.0	3.9	3.8	3.7	3.5	3.4	3.3	3.1	2.8

TABLE 112.—*Comparison of Baumé scales*

Percentage of sucrose or degrees Brix	Corresponding degrees Baume			Percentage of sucrose or degrees Brix	Corresponding degrees Baume		
	"New" scale (modulus 146.78)	"Old" scale (modulus 144)	NBS scale (modulus 145)		"New" scale (modulus 146.78)	"Old" scale (modulus 144)	NBS scale (modulus 145)
0	0.0	0.0	0.00	50	27.7	27.2	27.28
5	2.8	2.8	2.79	55	30.4	29.8	29.90
10	5.7	5.6	5.57	60	33.0	32.4	32.49
15	8.5	8.3	8.34	65	35.6	34.9	35.04
20	11.3	11.1	11.10	70	38.1	37.4	37.56
25	14.1	13.8	13.84	75	40.6	39.9	40.03
30	16.8	16.5	16.57	80	43.1	42.3	42.47
35	19.6	19.2	19.28	85	45.5	44.7	44.86
40	22.3	21.9	21.97	90	47.9	47.0	47.20
45	25.0	24.6	24.63	95	50.3	49.3	49.49
				100	----------	----------	51.73

TABLE 113.—*Density*[1] *of solutions of cane sugar at 20° C.*

[This table is the basis for standardizing hydrometers indicating percent of sugar at 20° C.]

Percentage of sugar	Tenths of percent				
	0	1	2	3	4
0	0. 998234	0. 998622	0. 999010	0. 999398	0. 999786
1	1. 002120	1. 002509	1. 002897	1. 003286	1. 003675
2	1. 006015	1. 006405	1. 006796	1. 007188	1. 007580
3	1. 009934	1. 010327	1. 010721	1. 011115	1. 011510
4	1. 013881	1. 014277	1. 014673	1. 015070	1. 015467
5	1. 017854	1. 018253	1. 018652	1. 019052	1. 019451
6	1. 021855	1. 022257	1. 022659	1. 023061	1. 023463
7	1. 025885	1. 026289	1. 026694	1. 027099	1. 027504
8	1. 029942	1. 030349	1. 030757	1. 031165	1. 031573
9	1. 034029	1. 034439	1. 034850	1. 035260	1. 035671
10	1. 038143	1. 038556	1. 038970	1. 039383	1. 039797
11	1. 042288	1. 042704	1. 043121	1. 043537	1. 043954
12	1. 046462	1. 046881	1. 047300	1. 047720	1. 048140
13	1. 050665	1. 051087	1. 051510	1. 051933	1. 052356
14	1. 054900	1. 055325	1. 055751	1. 056176	1. 056602
15	1. 059165	1. 059593	1. 060022	1. 060451	1. 060880
16	1. 063460	1. 063892	1. 064324	1. 064756	1. 065188
17	1. 067789	1. 068223	1. 068658	1. 069093	1. 069529
18	1. 072147	1. 072585	1. 073023	1. 073461	1. 073900
19	1. 076537	1. 076978	1. 077419	1. 077860	1. 078302
20	1. 080959	1. 081403	1. 081848	1. 082292	1. 082737
21	1. 085414	1. 085861	1. 086309	1. 086757	1. 087205
22	1. 089900	1. 090351	1. 090802	1. 091253	1. 091704
23	1. 094420	1. 094874	1. 095328	1. 095782	1. 096236
24	1. 098971	1. 099428	1. 099886	1. 100344	1. 100802
25	1. 103557	1. 104017	1. 104478	1. 104938	1. 105400
26	1. 108175	1. 108639	1. 109103	1. 109568	1. 110033
27	1. 112828	1. 113295	1. 113763	1. 114229	1. 114697
28	1. 117512	1. 117982	1. 118453	1. 118923	1. 119395
29	1. 122231	1. 122705	1. 123179	1. 123653	1. 124128
30	1. 126984	1. 127461	1. 127939	1. 128417	1. 128896
31	1. 131773	1. 132254	1. 132735	1. 133216	1. 133698
32	1. 136596	1. 137080	1. 137565	1. 138049	1. 138534
33	1. 141453	1. 141941	1. 142429	1. 142916	1. 143405
34	1. 146345	1. 146836	1. 147328	1. 147820	1. 148313
35	1. 151275	1. 151770	1. 152265	1. 152760	1. 153256
36	1. 156238	1. 156736	1. 157235	1. 157733	1. 158233
37	1. 161236	1. 161738	1. 162240	1. 162742	1. 163245
38	1. 166269	1. 166775	1. 167281	1. 167786	1. 168293
39	1. 171340	1. 171849	1. 172359	1. 172869	1. 173379
40	1. 176447	1. 176960	1. 177473	1. 177987	1. 178501
41	1. 181592	1. 182108	1. 182625	1. 183142	1. 183660
42	1. 186773	1. 187293	1. 187814	1. 188335	1. 188856
43	1. 191993	1. 192517	1. 193041	1. 193565	1. 194090
44	1. 197247	1. 197775	1. 198303	1. 198832	1. 199360

[1] According to F. Plato (Kaiserlichen Normal-Eichungs-Kommission, Wiss. Abh. 2, 153 (1900).

TABLE 113.—*Density of solutions of cane sugar at 20° C.*—Continued

Percentage of sugar	Tenths of percent				
	5	6	7	8	9
0	1. 000174	1. 000563	1. 000952	1. 001342	1. 001731
1	1. 004064	1. 004453	1. 004844	1. 005234	1. 005624
2	1. 007972	1. 008363	1. 008755	1. 009148	1. 009541
3	1. 011904	1. 012298	1. 012694	1. 013089	1. 013485
4	1. 015864	1. 016261	1. 016659	1. 017058	1. 017456
5	1. 019851	1. 020251	1. 020651	1. 021053	1. 021454
6	1. 023867	1. 024270	1. 024673	1. 025077	1. 025481
7	1. 027910	1. 028316	1. 028722	1. 029128	1. 029535
8	1. 031982	1. 032391	1. 032800	1. 033209	1. 033619
9	1. 036082	1. 036494	1. 036906	1. 037318	1. 037730
10	1. 040212	1. 040626	1. 041041	1. 041456	1. 041872
11	1. 044370	1. 044788	1. 045206	1. 045625	1. 046043
12	1. 048559	1. 048980	1. 049401	1. 049822	1. 050243
13	1. 052778	1. 053202	1. 053626	1. 054050	1. 054475
14	1. 057029	1. 057455	1. 057882	1. 058310	1. 058737
15	1. 061308	1. 061738	1. 062168	1. 062598	1. 063029
16	1. 065621	1. 066054	1. 066487	1. 066921	1. 067355
17	1. 069964	1. 070400	1. 070836	1. 071273	1. 071710
18	1. 074338	1. 074777	1. 075217	1. 075657	1. 076097
19	1. 078744	1. 079187	1. 079629	1. 080072	1. 080515
20	1. 083182	1. 083628	1. 084074	1. 084520	1. 084967
21	1. 087652	1. 088101	1. 088550	1. 089000	1. 089450
22	1. 092155	1. 092607	1. 093060	1. 093513	1. 093966
23	1. 096691	1. 097147	1. 097603	1. 098058	1. 098514
24	1. 101259	1. 101718	1. 102177	1. 102637	1. 103097
25	1. 105862	1. 106324	1. 106786	1. 107248	1. 107711
26	1. 110497	1. 110963	1. 111429	1. 111895	1. 112361
27	1. 115166	1. 115635	1. 116104	1. 116572	1. 117042
28	1. 119867	1. 120339	1. 120812	1. 121284	1. 121757
29	1. 124603	1. 125079	1. 125555	1. 126030	1. 126507
30	1. 129374	1. 129853	1. 130332	1. 130812	1. 131292
31	1. 134180	1. 134663	1. 135146	1. 135628	1. 136112
32	1. 139020	1. 139506	1. 139993	1. 140479	1. 140966
33	1. 143894	1. 144384	1. 144874	1. 145363	1. 145854
34	1. 148805	1. 149298	1. 149792	1. 150286	1. 150780
35	1. 153752	1. 154249	1. 154746	1. 155242	1. 155740
36	1. 158733	1. 159233	1. 159733	1. 160233	1. 160734
37	1. 163748	1. 164252	1. 164756	1. 165259	1. 165764
38	1. 168800	1. 169307	1. 169815	1. 170322	1. 170831
39	1. 173889	1. 174400	1. 174911	1. 175423	1. 175935
40	1. 179014	1. 179527	1. 180044	1. 180560	1. 181076
41	1. 184178	1. 184696	1. 185215	1. 185734	1. 186253
42	1. 189379	1. 189901	1. 190423	1. 190946	1. 191469
43	1. 194616	1. 195141	1. 195667	1. 196193	1. 196720
44	1. 199890	1. 200420	1. 200950	1. 201480	1. 202010

TABLE 113.—*Density of solutions of cane sugar at 20° C.*—Continued

Percentage of sugar	Tenths of percent				
	0	1	2	3	4
45	1. 202540	1. 203071	1. 203603	1. 204136	1. 204668
46	1. 207870	1. 208405	1. 208940	1. 209477	1. 210013
47	1. 213238	1. 213777	1. 214317	1. 214856	1. 215395
48	1. 218643	1. 219185	1. 219729	1. 220272	1. 220815
49	1. 224086	1. 224632	1. 225180	1. 225727	1. 226274
50	1. 229567	1. 230117	1. 230668	1. 231219	1. 231770
51	1. 235085	1. 235639	1. 236194	1. 236748	1. 237303
52	1. 240641	1. 241198	1. 241757	1. 242315	1. 242873
53	1. 246234	1. 246795	1. 247358	1. 247920	1. 248482
54	1. 251866	1. 252431	1. 252997	1. 253563	1. 254129
55	1. 257535	1. 258104	1. 258674	1. 259244	1. 259815
56	1. 263243	1. 263816	1. 264390	1. 264963	1. 265537
57	1. 268989	1. 269565	1. 270143	1. 270720	1. 271299
58	1. 274774	1. 275354	1. 275936	1. 276517	1. 277098
59	1. 280595	1. 281179	1. 281764	1. 282349	1. 282935
60	1. 286456	1. 287044	1. 287633	1. 288222	1. 288811
61	1. 292354	1. 292946	1. 293539	1. 294131	1. 294725
62	1. 298291	1. 298886	1. 299483	1. 300079	1. 300677
63	1. 304267	1. 304867	1. 305467	1. 306068	1. 306669
64	1. 310282	1. 310885	1. 311489	1. 312093	1. 312699
65	1. 316334	1. 316941	1. 317549	1. 318157	1. 318766
66	1. 322425	1. 323036	1. 323648	1. 324259	1. 324872
67	1. 328554	1. 329170	1. 329785	1. 330401	1. 331017
68	1. 334722	1. 335342	1. 335961	1. 336581	1. 337200
69	1. 340928	1. 341551	1. 342174	1. 342798	1. 343421
70	1. 347174	1. 347801	1. 348427	1. 349055	1. 349682
71	1. 353456	1. 354087	1. 354717	1. 355349	1. 355980
72	1. 359778	1. 360413	1. 361047	1. 361682	1. 362317
73	1. 366139	1. 366777	1. 367415	1. 368054	1. 368693
74	1. 372536	1. 373178	1. 373820	1. 374463	1. 375105
75	1. 378971	1. 379617	1. 380262	1. 380909	1. 381555
76	1. 385446	1. 386096	1. 386745	1. 387396	1. 388045
77	1. 391956	1. 392610	1. 393263	1. 393917	1. 394571
78	1. 398505	1. 399162	1. 399819	1. 400477	1. 401134
79	1. 405091	1. 405752	1. 406412	1. 407074	1. 407735
80	1. 411715	1. 412380	1. 413044	1. 413709	1. 414374
81	1. 418374	1. 419043	1. 419711	1. 420380	1. 421049
82	1. 425072	1. 425744	1. 426416	1. 427089	1. 427761
83	1. 431807	1. 432483	1. 433158	1. 433835	1. 434511
84	1. 438579	1. 439259	1. 439938	1. 440619	1. 441299
85	1. 445388	1. 446071	1. 446754	1. 447438	1. 448121
86	1. 452232	1. 452919	1. 453605	1. 454292	1. 454980
87	1. 459114	1. 459805	1. 460495	1. 461186	1. 461877
88	1. 466032	1. 466726	1. 467420	1. 468115	1. 468810
89	1. 472986	1. 473684	1. 474381	1. 475080	1. 475779

TABLE 113.—*Density of solutions of cane sugar at 20° C.*—Continued

Percentage of sugar	Tenths of percent				
	5	6	7	8	9
45	1. 205200	1. 205733	1. 206266	1. 206801	1. 207335
46	1. 210549	1. 211086	1. 211623	1. 212162	1. 212700
47	1. 215936	1. 216476	1. 217017	1. 217559	1. 218101
48	1. 221360	1. 221904	1. 222449	1. 222995	1. 223540
49	1. 226823	1. 227371	1. 227919	1. 228469	1. 229018
50	1. 232322	1. 232874	1. 233426	1. 233979	1. 234532
51	1. 237859	1. 238414	1. 238970	1. 239527	1. 240084
52	1. 243433	1. 243992	1. 244552	1. 245113	1. 245673
53	1. 249046	1. 249609	1. 250172	1. 250737	1. 251301
54	1. 254697	1. 255264	1. 255831	1. 256400	1. 256967
55	1. 260385	1. 260955	1. 261527	1. 262099	1. 262671
56	1. 266112	1. 266686	1. 267261	1. 267837	1. 268413
57	1. 271877	1. 272455	1. 273035	1. 273614	1. 274194
58	1. 277680	1. 278262	1. 278844	1. 279428	1. 280011
59	1. 283521	1. 284107	1. 284694	1. 285281	1. 285869
60	1. 289401	1. 289991	1. 290581	1. 291172	1. 291763
61	1. 295318	1. 295911	1. 296506	1. 297100	1. 297696
62	1. 301274	1. 301871	1. 302470	1. 303068	1. 303668
63	1. 307271	1. 307872	1. 308475	1. 309077	1. 309680
64	1. 313304	1. 313909	1. 314515	1. 315121	1. 315728
65	1. 319374	1. 319983	1. 320593	1. 321203	1. 321814
66	1. 325484	1. 326097	1. 326711	1. 327325	1. 327940
67	1. 331633	1. 332250	1. 332868	1. 333485	1. 334103
68	1. 337821	1. 338441	1. 339063	1. 339684	1. 340306
69	1. 344046	1. 344671	1. 345296	1. 345922	1. 346547
70	1. 350311	1. 350939	1. 351568	1. 352197	1. 352827
71	1. 356612	1. 357245	1. 357877	1. 358511	1. 359144
72	1. 362953	1. 363590	1. 364226	1. 364864	1. 365501
73	1. 369333	1. 369973	1. 370613	1. 371254	1. 371894
74	1. 375749	1. 376392	1. 377036	1. 377680	1. 378326
75	1. 382203	1. 382851	1. 383499	1. 384148	1. 384796
76	1. 388696	1. 389347	1. 389999	1. 390651	1. 391303
77	1. 395226	1. 395881	1. 396536	1. 397192	1. 397848
78	1. 401793	1. 403452	1. 403111	1. 403771	1. 404430
79	1. 408398	1. 409061	1. 409723	1. 410387	1. 411051
80	1. 415040	1. 415706	1. 416373	1. 417039	1. 417707
81	1. 421719	1. 422390	1. 423059	1. 423730	1. 424400
82	1. 428435	1. 429109	1. 429782	1. 430457	1. 431131
83	1. 435188	1. 435866	1. 436543	1. 437222	1. 437900
84	1. 441980	1. 442661	1. 443342	1. 444024	1. 444705
85	1. 448806	1. 449491	1. 450175	1. 450860	1. 451545
86	1. 455668	1. 456357	1. 457045	1. 457735	1. 458424
87	1. 462568	1. 463260	1. 463953	1. 464645	1. 465338
88	1. 469504	1. 470200	1. 470896	1. 471592	1. 472289
89	1. 476477	1. 477176	1. 477876	1. 478575	1. 479275

TABLE 113.—*Density of solutions of cane sugar at 20° C.*—Continued

Percentage of sugar	Tenths of percent				
	0	1	2	3	4
90	1. 479976	1. 480677	1. 481378	1. 482080	1. 482782
91	1. 487002	1. 487707	1. 488411	1. 489117	1. 489823
92	1. 494063	1. 494771	1. 495479	1. 496188	1. 496897
93	1. 501158	1. 501870	1. 502582	1. 503293	1. 504006
94	1. 508289	1. 509004	1. 509720	1. 510435	1. 511151
95	1. 515455	1. 516174	1. 516893	1. 517612	1. 518332
96	1. 522656	1. 523378	1. 524100	1. 524823	1. 525546
97	1. 529891	1. 530616	1. 531342	1. 532068	1. 532794
98	1. 537161	1. 537889	1. 538618	1. 539347	1. 540076
99	1. 544462	1. 545194	1. 545926	1. 546659	1. 547392
100	1. 551800				

TABLE 113.—*Density of solutions of cane sugar at 20° C.*—Continued

Percentage of sugar	Tenths of percent				
	5	6	7	8	9
90	1. 483484	1. 484187	1. 484890	1. 485593	1. 486297
91	1. 490528	1. 491234	1. 491941	1. 492647	1. 493355
92	1. 497606	1. 498316	1. 499026	1. 499736	1. 500447
93	1. 504719	1. 505432	1. 506146	1. 506859	1. 507574
94	1. 511868	1. 512585	1. 513302	1. 514019	1. 514737
95	1. 519051	1. 519771	1. 520492	1. 521212	1. 521934
96	1. 526269	1. 526993	1. 527717	1. 528441	1. 529166
97	1. 533521	1. 534248	1. 534976	1. 535704	1. 536432
98	1. 540806	1. 541536	1. 542267	1. 542998	1. 543730
99	1. 548127	1. 548861	1. 549595	1. 550329	1. 551064
100	----------	----------	----------	----------	----------

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*.

Column 1 gives Brix or percentage of sucrose in the solution.

Column 2 gives apparent density, that is, the weight in air with brass weights of 1 ml of solution at 20° C. The values in this column correspond to the values of true density (table 113), having been obtained by means of the formula

$$M = W\left[1 + \frac{\rho}{d_2}\left(\frac{d_2 - d_1}{d_1 - \rho}\right)\right] = W\left(1 + \frac{k}{1000}\right),^{1}$$

which may be utilized for converting apparent density into true density, and vice versa, by considering that M, the weight in vacuo, and W, the apparent weight, refer to 1 ml, since true density is defined as the weight in vacuo of 1 ml, and the apparent density as the weight of 1 ml of substance in air with brass weights. ρ is the density of air, which has been taken as 0.0012046;[2] d_1 the density of the solution, d_2 the density of the weights, which has been taken as 8.4.

Column 3 gives the apparent specific gravity at 20° C. The values in this column were obtained by dividing the apparent density in column 2 by the apparent density of water at 20° C., which was taken as 0.997174.[3]

Column 4 gives the grams sucrose (weighed in vacuo) per 100 ml of solution.

The values in the table were calculated in three sections by different individuals; thus from 40 to 60 Brix by Peters and Phelps (BS Tech. Paper T338, 1927); 60 to 83.9 Brix by Brewster and Phelps (NBS Research Paper RP536, 1933); and the remaining values, 0 to 40 and 84 to 95 Brix by Snyder, Saunders, and Golden of this Bureau. After the computations were completed, the tabulations were made by rounding off the values to the last figure given. The values are considered exact to ±1 in the fifth decimal.

Percentage of sucrose by weight (Brix)[4]	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
0. 0	0. 99717	1. 00000	0. 000	2. 0	1. 00495	1. 00780	2. 012
. 1	. 99756	. 00039	. 100	. 1	. 00534	. 00819	. 113
. 2	. 99795	. 00078	. 200	. 2	. 00574	. 00859	. 215
. 3	. 99834	. 00117	. 300	. 3	. 00613	. 00898	. 317
. 4	. 99872	. 00156	. 400	. 4	. 00652	. 00937	. 418
. 5	. 99911	. 00194	. 500	. 5	. 00691	. 00977	. 520
. 6	. 99950	. 00233	. 600	. 6	. 00730	. 01016	. 622
. 7	. 99989	. 00272	. 701	. 7	. 00769	. 01055	. 724
. 8	1. 00028	. 00312	. 801	. 8	. 00809	. 01094	. 826
. 9	. 00067	. 00351	. 902	. 9	. 00848	. 01134	. 928
1. 0	1. 00106	1. 00390	1. 002	3. 0	1. 00887	1. 01173	3. 030
. 1	. 00145	. 00429	. 103	. 1	. 00927	. 01213	. 132
. 2	. 00184	. 00468	. 203	. 2	. 00966	. 01252	. 234
. 3	. 00223	. 00507	. 304	. 3	. 01006	. 01292	. 337
. 4	. 00261	. 00546	. 405	. 4	. 01045	. 01331	. 439
. 5	. 00300	. 00585	. 506	. 5	. 01084	. 01371	. 542
. 6	. 00339	. 00624	. 607	. 6	. 01124	. 01410	. 644
. 7	. 00378	. 00663	. 708	. 7	. 01163	. 01450	. 747
. 8	. 00417	. 00702	. 809	. 8	. 01203	. 01490	. 850
. 9	. 00456	. 00741	. 911	. 9	. 01243	. 01529	. 953

[1] NBS Circular C19, 6th ed., table 39, p. 55 (1924).
[2] NBS Circular C19, 6th ed., table 29 (1924).
[3] J. Domke, Z. ver. deut. Zuckerind. 62, 306 (1912); O. Schrefeld, p. 312.
[4] The apparent Brix, that is, grams of sucrose dry substance per 100 g of solution, weighed with brass weights in air, is approximately 0.01 percent greater than the true Brix in column 1.

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
4. 0	1. 01282	1. 01569	4. 056	9. 0	1. 03297	1. 03590	9. 306
. 1	. 01322	. 01609	. 159	. 1	. 03338	. 03631	. 413
. 2	. 01361	. 01649	. 262	. 2	. 03379	. 03672	. 521
. 3	. 01401	. 01688	. 365	. 3	. 03420	. 03713	. 628
. 4	. 01441	. 01728	. 468	. 4	. 03461	. 03755	. 735
. 5	. 01480	. 01768	. 571	. 5	. 03503	. 03796	. 843
. 6	. 01520	. 01808	. 675	. 6	. 03544	. 03837	. 950
. 7	. 01560	. 01848	. 778	. 7	. 03585	. 03879	10. 058
. 8	. 01600	. 01888	. 882	. 8	. 03626	. 03920	. 166
. 9	. 01640	. 01928	. 986	. 9	. 03667	. 03961	. 274
5. 0	1. 01680	1. 01968	5. 089	10. 0	1. 03709	1. 04003	10. 381
. 1	. 01719	. 02008	. 193	. 1	. 03750	. 04044	. 489
. 2	. 01759	. 02048	. 297	. 2	. 03791	. 04086	. 597
. 3	. 01799	. 02088	. 401	. 3	. 03833	. 04127	. 706
. 4	. 01839	. 02128	. 506	. 4	. 03874	. 04169	. 814
. 5	. 01879	. 02168	. 609	. 5	. 03916	. 04210	. 922
. 6	. 01919	. 02208	. 713	. 6	. 03957	. 04252	11. 031
. 7	. 01959	. 02248	. 818	. 7	. 03999	. 04293	. 139
. 8	. 01999	. 02289	. 922	. 8	1. 04040	. 04335	. 248
. 9	. 02040	. 02329	6. 027	. 9	. 04082	. 04377	. 356
6. 0	1. 02080	1. 02369	6. 131	11. 0	1. 04123	1. 04418	11. 465
. 1	. 02120	. 02409	. 236	. 1	. 04165	. 04460	. 574
. 2	. 02160	. 02450	. 340	. 2	. 04207	. 04502	. 683
. 3	. 02200	. 02490	. 445	. 3	. 04248	. 04544	. 792
. 4	. 02241	. 02530	. 550	. 4	. 04290	. 04585	. 901
. 5	. 02281	. 02571	. 655	. 5	. 04332	. 04627	12. 010
. 6	. 02321	. 02611	. 760	. 6	. 04373	. 04669	. 120
. 7	. 02362	. 02652	. 865	. 7	. 04415	. 04711	. 229
. 8	. 02402	. 02692	. 971	. 8	. 04457	. 04753	. 338
. 9	. 02442	. 02733	7. 076	. 9	. 04499	. 04795	. 448
7. 0	1. 02483	1. 02773	7. 181	12. 0	1, 04541	1. 04837	12. 558
. 1	. 02523	. 02814	. 287	. 1	. 04583	. 04879	. 667
. 2	. 02564	. 02854	. 392	. 2	. 04625	. 04921	. 777
. 3	. 02604	. 02895	. 498	. 3	. 04667	. 04963	. 887
. 4	. 02645	. 20936	. 604	. 4	. 04709	1. 05005	. 997
. 5	. 02685	. 02976	. 709	. 5	. 04750	. 05047	13. 107
. 6	. 02726	. 03017	. 815	. 6	. 04793	. 05090	. 217
. 7	. 02766	. 03058	. 921	. 7	. 04835	. 05132	. 327
. 8	. 02807	. 03098	8. 027	. 8	. 04877	. 05174	. 438
. 9	. 02848	. 03139	. 133	. 9	. 04919	. 05216	. 548
8. 0	1. 02888	1. 03180	8. 240	13. 0	1. 04961	1. 05259	13. 659
. 1	. 02929	. 03221	. 346	. 1	1. 05003	. 05301	. 769
. 2	. 02970	. 03262	. 452	. 2	. 05046	. 05343	. 880
. 3	. 03011	. 03303	. 559	. 3	. 05088	. 05386	. 991
. 4	. 03052	. 03344	. 665	. 4	. 05130	. 05428	14. 102
. 5	. 03093	. 03385	. 772	. 5	. 05172	. 05470	. 213
. 6	. 03133	. 03426	. 879	. 6	. 05215	. 05513	. 324
. 7	. 03174	. 03467	. 985	. 7	. 05257	. 05556	. 435
. 8	. 03215	. 03508	9. 092	. 8	. 05300	. 05598	. 546
. 9	. 03256	. 03549	. 199	. 9	. 05342	. 05641	. 657

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
14. 0	1. 05385	1. 05683	14. 769	19. 0	1. 07549	1. 07853	20. 454
. 1	. 05427	. 05726	. 880	. 1	. 07593	. 07898	. 570
. 2	. 05470	. 05769	. 992	. 2	. 07637	. 07942	. 686
. 3	. 05512	. 05811	15. 103	. 3	. 07681	. 07986	. 803
. 4	. 05555	. 05854	. 215	. 4	. 07725	1. 08030	. 919
. 5	. 05598	. 05897	. 327	. 5	. 07769	. 08075	21. 036
. 6	. 05640	. 05940	. 439	. 6	. 07814	. 08119	. 152
. 7	. 05683	. 05982	. 551	. 7	. 07858	. 08164	. 269
. 8	. 05726	1. 06025	. 663	. 8	. 07902	. 08208	. 385
. 9	. 05768	. 06068	. 775	. 9	. 07947	. 08252	. 502
15. 0	1. 05811	1. 06111	15. 887	20. 0	1. 07991	1. 08297	21. 619
. 1	. 05854	. 06154	16. 000	. 1	1. 08035	. 08342	. 736
. 2	. 05897	. 06197	. 112	. 2	. 08080	. 08386	. 853
. 3	. 05940	. 06240	. 225	. 3	. 08124	. 08431	. 971
. 4	. 05983	. 06283	. 338	. 4	. 08169	. 08475	22. 088
. 5	1. 06026	. 06326	. 450	. 5	. 08213	. 08520	. 205
. 6	. 06069	. 06369	. 563	. 6	. 08258	. 08565	. 323
. 7	. 06112	. 06412	. 676	. 7	. 08302	. 08609	. 440
. 8	. 06155	. 06455	. 789	. 8	. 08347	. 08654	. 558
. 9	. 06198	. 06499	. 902	. 9	. 08392	. 08699	. 676
16. 0	1. 06241	1. 06542	17. 015	21. 0	1. 08436	1. 08744	22. 794
. 1	. 06284	. 06585	. 129	. 1	. 08481	. 08789	. 912
. 2	. 06327	. 06629	. 242	. 2	. 08526	. 08834	23. 030
. 3	. 06370	. 06672	. 356	. 3	. 08571	. 08879	. 148
. 4	. 06414	. 06715	. 469	. 4	. 08616	. 08923	. 266
. 5	. 06457	. 06759	. 583	. 5	. 08660	. 08968	. 385
. 6	. 06500	. 06802	. 697	. 6	. 08705	1. 09013	. 503
. 7	. 06544	. 06845	. 810	. 7	. 08750	. 09058	. 622
. 8	. 06587	. 06889	. 924	. 8	. 08795	. 09103	. 740
. 9	. 06630	. 06933	18. 038	. 9	. 08840	. 09149	. 859
17. 0	1. 06674	1. 06976	18. 152	22. 0	1. 08885	1. 09194	23. 978
. 1	. 06717	1. 07020	. 267	. 1	. 08930	. 09239	24. 097
. 2	. 06761	. 07063	. 381	. 2	. 08975	. 09284	. 216
. 3	. 06804	. 07107	. 495	. 3	1. 09020	. 09329	. 335
. 4	. 06848	. 07151	. 610	. 4	. 09066	. 09375	. 454
. 5	. 06891	. 07194	. 724	. 5	. 09111	. 09420	. 573
. 6	. 06935	. 07238	. 839	. 6	. 09156	. 09465	. 693
. 7	. 06978	. 07282	. 954	. 7	. 09201	. 09511	. 812
. 8	1. 07022	. 07325	19. 069	. 8	. 09247	. 09556	. 932
. 9	. 07066	. 07369	. 184	. 9	. 09292	. 09602	25. 052
18. 0	1. 07110	1. 07413	19. 299	23. 0	1. 09337	1. 09647	25. 172
. 1	. 07153	. 07457	. 414	. 1	. 09383	. 09693	. 292
. 2	. 07197	. 07501	. 529	. 2	. 09428	. 09738	. 412
. 3	. 07241	. 07545	. 644	. 3	. 09473	. 09784	. 532
. 4	. 07285	. 07589	. 760	. 4	. 09519	. 09829	. 652
. 5	. 07329	. 07633	. 875	. 5	. 09564	. 09875	. 772
. 6	. 07373	. 07677	. 991	. 6	. 09610	. 09921	. 893
. 7	. 07417	. 07721	20. 107	. 7	. 09656	1. 09966	26. 013
. 8	. 07461	. 07765	. 222	. 8	. 09701	1. 10012	. 134
. 9	. 07505	. 07809	. 338	. 9	. 09747	. 10058	. 255

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
24. 0	1. 09792	1. 10104	26. 375	29. 0	1. 12119	1. 12436	32. 545
. 1	. 09838	. 10149	. 496	. 1	. 12166	. 12484	. 671
. 2	. 09884	. 10195	. 617	. 2	. 12214	. 12532	. 797
. 3	. 09930	. 10241	. 738	. 3	. 12261	. 12579	. 923
. 4	. 09976	. 10287	. 860	. 4	. 12308	. 12627	33. 049
. 5	1. 10021	. 10333	. 981	. 5	. 12356	. 12674	. 176
. 6	. 10067	. 10379	27. 102	. 6	. 12404	. 12722	. 302
. 7	. 10113	. 10425	. 224	. 7	. 12451	. 12770	. 429
. 8	. 10159	. 10471	. 345	. 8	. 12499	. 12817	. 556
. 9	. 10205	. 10517	. 467	. 9	. 12546	. 12865	. 683
25. 0	1. 10251	1. 10564	27. 589	30. 0	1. 12594	1. 12913	33. 810
. 1	. 10297	. 10610	. 710	. 1	. 12642	. 12961	. 937
. 2	. 10343	. 10656	. 833	. 2	. 12690	1. 13009	34. 064
. 3	. 10389	. 10702	. 955	. 3	. 12737	. 13057	. 191
. 4	. 10435	. 10748	28. 077	. 4	. 12785	. 13105	. 318
. 5	. 10482	. 10795	. 199	. 5	. 12833	. 13153	. 446
. 6	. 10528	. 10841	. 322	. 6	. 12881	. 13201	. 574
. 7	. 10574	. 10887	. 444	. 7	. 12929	. 13249	. 701
. 8	. 10620	. 10934	. 567	. 8	. 12977	. 13297	. 829
. 9	. 10667	. 10980	. 690	. 9	1. 13025	. 13345	. 957
26. 0	1. 10713	1. 11027	28. 813	31. 0	1. 13073	1. 13394	35. 085
. 1	. 10759	. 11073	. 935	. 1	. 13121	. 13442	. 213
. 2	. 10806	. 11120	29. 059	. 2	. 13169	. 13490	. 341
. 3	. 10852	. 11166	. 182	. 3	. 13217	. 13538	. 470
. 4	. 10899	. 11213	. 305	. 4	. 13266	. 13587	. 598
. 5	. 10945	. 11260	. 428	. 5	. 13314	. 13635	. 727
. 6	. 10992	. 11306	. 552	. 6	. 13362	. 13683	. 855
. 7	1. 11038	. 11353	. 675	. 7	. 13410	. 13732	. 984
. 8	. 11085	. 11400	. 799	. 8	. 13459	. 13780	36. 113
. 9	. 11131	. 11447	. 923	. 9	. 13507	. 13829	. 242
27. 0	1. 11178	1. 11493	30. 046	32. 0	1. 13555	1. 13877	36. 371
. 1	. 11225	. 11540	. 170	. 1	. 13604	. 13926	. 500
. 2	. 11272	. 11587	. 294	. 2	. 13652	. 13974	. 630
. 3	. 11318	. 11634	. 418	. 3	. 13701	1. 14023	. 759
. 4	. 11365	. 11681	. 543	. 4	. 13749	. 14072	. 889
. 5	. 11412	. 11728	. 667	. 5	. 13798	. 14120	37. 018
. 6	. 11459	. 11775	. 792	. 6	. 13846	. 14169	. 148
. 7	. 11506	. 11822	. 916	. 7	. 13895	. 14218	. 278
. 8	. 11553	. 11869	31. 041	. 8	. 13944	. 14267	. 408
. 9	. 11600	. 11916	. 165	. 9	. 13992	. 14316	. 538
28. 0	1. 11647	1. 11963	31. 290	33. 0	1. 14041	1. 14364	37. 668
. 1	. 11694	1. 12010	. 415	. 1	. 14090	. 14413	. 798
. 2	. 11741	. 12058	. 540	. 2	. 14139	. 14462	. 929
. 3	. 11788	. 12105	. 666	. 3	. 14188	. 14511	38. 059
. 4	. 11835	. 12152	. 791	. 4	. 14236	. 14560	. 190
. 5	. 11882	. 12199	. 916	. 5	. 14285	. 14609	. 320
. 6	. 11929	. 12247	32. 042	. 6	. 14334	. 14658	. 451
. 7	. 11977	. 12294	. 167	. 7	. 14383	. 14708	. 582
. 8	1. 12024	. 12341	. 293	. 8	. 14432	. 14757	. 713
. 9	. 12071	. 12389	. 419	. 9	. 14481	. 14806	. 844

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
34. 0	1. 14530	1. 14855	38. 976	39. 0	1. 17030	1. 17362	45. 682
. 1	. 14580	. 14904	39. 107	. 1	. 17081	. 17413	. 819
. 2	. 14629	. 14954	. 239	. 2	. 17132	. 17464	. 956
. 3	. 14678	1. 15003	. 370	. 3	. 17183	. 17515	46. 094
. 4	. 14727	. 15052	. 502	. 4	. 17234	. 17566	. 231
. 5	. 14776	. 15102	. 634	. 5	. 17285	. 17618	. 369
. 6	. 14826	. 15151	. 767	. 6	. 17336	. 17669	. 506
. 7	. 14875	. 15201	. 898	. 7	. 17387	. 17720	. 644
. 8	. 14925	. 15250	40. 030	. 8	. 17439	. 17772	. 782
. 9	. 14974	. 15300	. 162	. 9	. 17490	. 17823	. 920
35. 0	1. 15024	1. 15350	40. 295	40. 0	1. 17541	1. 17874	47. 058
. 1	. 15073	. 15399	. 427	40. 1	593	926	. 196
. 2	. 15123	. 15449	. 560	40. 2	644	1. 17977	. 334
. 3	. 15172	. 15498	. 692	40. 3	695	1. 18029	. 473
. 4	. 15222	. 15548	. 825	40. 4	747	080	. 611
. 5	. 15271	. 15598	. 958	40. 5	1. 17798	1. 18132	. 750
. 6	. 15321	. 15648	41. 091	40. 6	849	183	47. 889
. 7	. 15371	. 15698	. 224	40. 7	901	235	48. 028
. 8	. 15420	. 15747	. 358	40. 8	1. 17953	287	. 167
. 9	. 15470	. 15797	. 491	40. 9	1. 18004	339	. 306
36. 0	1. 15520	1. 15847	41. 625	41. 0	1. 18056	1. 18390	48. 445
. 1	. 15570	. 15897	. 758	41. 1	107	442	. 585
. 2	. 15620	. 15947	. 892	41. 2	159	494	. 724
. 3	. 15669	. 15597	42. 026	41. 3	211	546	. 864
. 4	. 15719	1. 16047	. 160	41. 4	263	598	49. 004
. 5	. 15769	. 16098	. 294	41. 5	1. 18314	1. 18650	. 143
. 6	. 15819	. 16148	. 428	41. 6	356	702	. 283
. 7	. 15869	. 16198	. 562	41. 7	418	754	. 424
. 8	. 15919	. 16248	. 697	41. 8	470	806	. 564
. 9	. 15970	. 16298	. 831	41. 9	522	858	. 704
37. 0	1. 16020	1. 16349	42. 966	42. 0	1. 18574	1. 18910	49. 845
. 1	. 16070	. 16399	43. 100	42. 1	626	1. 18962	49. 985
. 2	. 16120	. 16449	. 235	42. 2	678	1. 19014	50. 126
. 3	. 16170	. 16500	. 376	42. 3	730	062	. 267
. 4	. 16221	. 16550	. 500	42. 4	782	119	50. 408
. 5	. 16271	. 16601	. 645	42. 5	1. 18835	1. 19171	. 549
. 6	. 16321	. 16651	. 771	42. 6	887	224	. 690
. 7	. 16372	. 16702	. 911	42. 7	939	276	. 831
. 8	. 16422	. 16752	44. 047	42 8	991	329	50. 973
. 9	. 16473	. 16803	. 182	42. 9	1. 19044	381	51. 114
38. 0	1. 16523	1. 16853	44. 318	43. 0	1. 19096	1. 19434	51. 256
. 1	. 16574	. 16904	. 454	43. 1	148	486	. 398
. 2	. 16624	. 16955	. 590	43. 2	201	539	. 539
. 3	. 16675	1. 17006	. 726	43. 3	253	591	. 681
. 4	. 16726	. 17056	. 862	43. 4	306	644	. 824
. 5	. 16776	. 17107	. 999	43. 5	1. 19358	1. 19697	51. 966
. 6	. 16827	. 17158	45. 135	43. 6	411	749	52. 108
. 7	. 16878	. 17209	. 272	43. 7	483	802	. 251
. 8	. 16929	. 17260	. 408	43. 8	516	855	. 393
. 9	. 16979	. 17311	. 545	43. 9	569	908	. 536

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
44. 0	1. 19622	1. 19961	52. 679	49. 0	1. 22306	1. 22652	59. 980
44. 1	674	1. 20013	. 822	49. 1	360	707	60. 129
44. 2	727	066	52. 965	49. 2	415	762	. 279
44. 3	780	119	53. 108	49. 3	470	817	. 428
44. 4	833	172	. 252	49. 4	525	872	. 578
44. 5	1. 19886	1. 20226	. 395	49. 5	1. 22580	1. 22927	. 728
44. 6	939	279	. 539	49. 6	634	1 22982	60. 878
44. 7	992	332	. 683	49. 7	689	1. 23037	61. 028
44. 8	1. 20045	385	. 826	49. 8	744	092	. 178
44. 9	098	438	53. 970	49. 9	799	147	61. 328
45. 0	1. 20151	1. 20491	54. 114	50. 0	1. 22854	1. 23202	61. 478
45. 1	204	545	. 259	50. 1	909	1. 23257	. 629
45. 2	257	598	. 403	50. 2	1. 22964	313	. 780
45. 3	311	651	. 547	50. 3	1. 23019	368	. 930
45. 4	364	705	. 692	50. 4	074	423	62. 081
45. 5	1. 20417	1. 20758	. 837	50. 5	1. 23130	1. 23478	. 232
45. 6	470	812	54. 981	50. 6	185	534	. 383
45. 7	524	865	55. 126	50. 7	240	589	. 535
45. 8	577	919	. 272	50. 8	295	645	. 686
45. 9	630	1. 20972	. 417	50. 9	351	700	. 838
46. 0	1. 20684	1. 21026	55. 562	51. 0	1. 23406	1. 23756	62. 989
46. 1	737	080	. 708	51. 1	461	811	63. 141
46. 2	791	133	. 853	51. 2	517	867	. 293
46. 3	845	187	55. 999	51. 3	572	922	. 445
46. 4	898	241	56. 145	51. 4	628	1. 23978	. 597
46. 5	1. 20952	1. 21295	. 291	51. 5	1. 23683	1. 24034	. 750
46. 6	1. 21006	349	. 437	51. 6	739	089	. 902
46. 7	059	402	. 583	51. 7	794	145	64. 055
46. 8	113	456	. 729	51. 8	850	201	. 208
46. 9	167	510	56. 876	51. 9	906	257	. 360
47. 0	1. 21221	1. 21564	57. 022	52. 0	1 23962	1. 24313	64. 513
47. 1	275	618	. 169	52. 1	1. 24017	369	. 666
47. 2	329	673	. 316	52. 2	073	425	. 820
47. 3	383	727	. 463	52. 3	129	481	. 973
47. 4	437	781	57. 610	52. 4	185	537	65. 127
47. 5	1. 21491	1. 21835	57. 757	52. 5	1. 24241	1. 24593	65. 280
47. 6	545	889	57. 904	52. 6	297	649	. 433
47. 7	599	943	58. 052	52. 7	353	705	. 588
47. 8	653	1. 21998	. 199	52. 8	409	761	. 742
47. 9	707	1. 22052	. 347	52. 9	465	818	. 896
48. 0	1. 21761	1. 22106	58. 495	53. 0	1. 24521	1. 24874	66. 050
48. 1	816	161	. 643	53. 1	577	930	. 205
48. 2	870	215	. 791	53. 2	633	987	. 359
48. 3	924	270.	58. 939	53. 3	690	1. 25043	. 514
48. 4	979	324	59. 087	53. 4	746	099	. 669
48. 5	1. 22033	1. 22379	. 236	53. 5	1. 24802	1. 25156	. 824
48. 6	088	434	. 385	53. 6	858	212	. 979
48. 7	142	488	. 533	53. 7	915	269	67. 134
48. 8	197	543	. 682	53. 8	971	325	. 290
48. 9	251	598	. 831	53. 9	1. 25028	382	. 445

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TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
54. 0	1. 25084	1. 25439	67. 601	59. 0	1. 27958	1. 28320	75. 555
54. 1	141	495	. 757	59. 1	1. 28017	379	. 718
54. 2	197	552	. 912	59. 2	075	437	. 880
54. 3	254	609	68. 069	59. 3	134	497	76. 043
54. 4	311	666	. 225	59. 4	193	556	. 207
54. 5	1. 25367	1. 25723	. 381	59. 5	251	614	. 369
54. 6	424	780	. 537	59. 6	309	672	. 533
54. 7	481	836	. 694	59. 7	367	731	. 696
54. 8	538	893	. 851	59. 8	426	789	. 860
54. 9	594	950	69. 008	59. 9	485	849	77. 024
55. 0	1. 25651	1. 26007	69. 164	60. 0	1. 28544	1. 28908	77. 188
55. 1	708	064	. 322	60. 1	602	966	. 351
55. 2	765	122	. 479	60. 2	661	1. 29025	. 515
55. 3	822	179	. 636	60. 3	720	084	. 680
55. 4	879	236	. 794	60. 4	779	143	. 844
55. 5	1. 25936	1. 26293	69. 951	60. 5	838	203	78. 009
55. 6	1. 25993	350	70. 109	60. 6	897	262	. 173
55. 7	1. 26050	408	. 267	60. 7	956	321	. 338
55. 8	108	465	. 425	60. 8	1. 29015	380	. 503
55. 9	165	522	. 583	60. 9	074	439	. 668
56. 0	1. 26222	1. 26580	70. 742	61. 0	1. 29133	1. 29498	78. 833
56. 1	279	637	70. 900	61. 1	193	559	. 999
56. 2	337	695	71. 059	61. 2	252	618	79. 165
56. 3	394	752	. 217	61. 3	311	677	. 330
56. 4	452	810	. 376	61. 4	370	736	. 496
56. 5	1. 26509	1. 26868	. 535	61. 5	430	796	. 662
56. 6	566	925	. 694	61. 6	489	855	. 828
56. 7	624	1. 26983	71. 854	61. 7	548	915	. 995
56. 8	682	1. 27041	72. 013	61. 8	608	975	80. 161
56. 9	739	098	. 173	61. 9	667	1. 30034	. 328
57. 0	1. 26797	1. 27156	72. 332	62. 0	1. 29726	1. 30093	80. 494
57. 1	854	214	. 492	62. 1	786	153	. 661
57. 2	912	272	. 652	62. 2	845	212	. 828
57. 3	970	330	. 812	62. 3	905	273	. 995
57. 4	1. 27028	388	72. 973	62. 4	966	334	81. 162
57. 5	1. 27086	1. 27446	73. 133	62. 5	1. 30025	393	. 329
57. 6	143	504	. 293	62. 6	085	453	. 497
57. 7	201	562	. 454	62. 7	145	513	. 665
57. 8	259	620	. 615	62. 8	205	573	. 833
57. 9	317	678	. 776	62. 9	265	633	82. 001
58. 0	1. 27375	1. 27736	73. 937	63. 0	1. 30325	1. 30694	82. 169
58. 1	433	794	74. 098	63. 1	385	754	. 337
58. 2	492	853	. 260	63. 2	446	815	. 506
58. 3	550	911	. 421	63. 3	506	875	. 674
58. 4	608	1. 27969	. 583	63. 4	566	936	. 843
58. 5	1. 27664	1. 28028	. 744	63. 5	626	994	83. 012
58. 6	724	086	74. 906	63. 6	686	1. 31055	. 180
58. 7	782	145	75. 068	63. 7	747	117	. 350
58. 8	841	203	. 230	63. 8	807	177	. 519
58. 9	899	262	. 393	63. 9	867	237	. 688

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
64. 0	1. 30927	1. 31297	83. 858	69. 0	1. 33992	1. 34371	92. 524
64. 1	988	359	84. 028	69. 1	1. 34054	433	. 701
64. 2	1. 31048	418	. 198	69. 2	116	495	. 878
64. 3	108	479	. 367	69. 3	179	558	93. 056
64. 4	169	540	. 538	69. 4	241	621	. 233
64. 5	229	600	. 708	69. 5	304	684	. 411
64. 6	290	661	. 879	69. 6	366	746	. 589
64. 7	350	723	85. 049	69. 7	429	809	. 767
64. 8	412	784	. 220	69. 8	491	871	. 945
64. 9	473	845	. 391	69. 9	554	934	94. 123
65. 0	1. 31533	1. 31905	85. 561	70. 0	1. 34616	1. 34997	94. 302
65. 1	594	966	. 733	70. 1	679	1. 35060	. 481
65. 2	655	1. 32028	. 904	70. 2	742	123	. 660
65. 3	716	089	86. 076	70. 3	805	186	. 839
65. 4	777	150	. 248	70. 4	867	248	95. 017
65. 5	837	210	. 419	70. 5	930	311	. 197
65. 6	898	271	. 591	70. 6	993	375	. 376
65. 7	959	332	. 763	70. 7	1. 35056	438	. 556
65. 8	1. 32019	393	. 935	70. 8	119	501	. 736
65. 9	081	455	87. 107	70. 9	182	564	. 916
66. 0	1. 32142	1. 32516	87. 280	71. 0	1. 35245	1. 35627	96. 096
66. 1	203	577	. 453	71. 1	308	691	. 276
66. 2	264	638	. 626	71. 2	371	754	. 456
66. 3	325	699	. 798	71. 3	434	817	. 636
66. 4	385	759	. 971	71. 4	498	881	. 817
66. 5	446	820	88. 142	71. 5	561	944	. 998
66. 6	509	884	. 318	71. 6	625	1. 36008	97. 179
66. 7	570	945	. 492	71. 7	688	072	. 360
66. 8	632	1. 33007	. 666	71. 8	751	135	. 541
66. 9	693	068	. 839	71. 9	814	198	. 722
67. 0	1. 32754	1. 33129	89. 012	72. 0	1. 35877	1. 36261	97. 904
67. 1	816	192	. 187	72. 1	940	324	98. 085
67. 2	878	254	. 361	72. 2	1. 36004	389	. 268
67. 3	939	315	. 536	72. 3	067	452	. 449
67. 4	1. 33001	377	. 711	72. 4	131	516	. 632
67. 5	062	438	. 885	72. 5	194	579	. 814
67. 6	124	500	90. 060	72. 6	258	643	. 997
67. 7	186	562	. 235	72. 7	322	707	99. 179
67. 8	248	625	. 411	72. 8	385	771	. 362
67. 9	309	686	. 585	72. 9	450	836	. 545
68. 0	1. 33371	1. 33748	90. 761	73. 0	1. 36514	1. 36900	99. 728
68. 1	433	810	. 937	73. 1	578	964	. 912
68. 2	495	872	91. 112	73. 2	642	1. 37028	100. 095
68. 3	557	935	. 288	73. 3	705	092	. 278
68. 4	619	997	. 464	73. 4	769	156	. 462
68. 5	681	1. 34059	. 641	73. 5	833	220	. 646
68. 6	743	121	. 817	73. 6	896	283	. 827
68. 7	805	183	. 993	73. 7	960	347	101. 014
68. 8	867	245	92. 169	73. 8	1. 37024	411	. 198
68. 9	930	309	. 347	73. 9	088	476	. 383

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
74. 0	1. 37153	1. 37541	101. 568	79. 0	1. 40409	1. 40806	111. 002
74. 1	217	605	. 753	79. 1	475	872	. 195
74. 2	281	669	. 937	79. 2	541	938	. 388
74. 3	345	733	102. 122	79. 3	607	1. 41005	. 581
74. 4	410	798	. 308	79. 4	674	072	. 775
74. 5	475	864	. 493	79. 5	740	138	. 968
74. 6	539	928	. 679	79. 6	806	204	112. 161
74. 7	604	993	. 865	79. 7	872	270	. 354
74. 8	668	1. 38057	103. 050	79. 8	939	337	. 549
74. 9	733	122	. 237	79. 9	1. 41005	404	. 743
75. 0	1. 37797	1. 38187	103. 423	80. 0	1. 41072	1. 41471	112. 938
75. 1	862	252	. 609	80. 1	138	537	113. 131
75. 2	926	316	. 796	80. 2	204	603	. 326
75. 3	991	381	. 983	80. 3	271	670	. 521
75. 4	055	445	104. 170	80. 4	337	737	. 715
75. 5	1. 38119	1. 38510	104. 356	80. 5	404	804	. 911
75. 6	184	575	. 543	80. 6	472	872	114. 106
75. 7	249	640	. 731	80. 7	537	937	. 301
75. 8	314	705	. 919	80. 8	604	1. 42004	. 497
75. 9	379	770	105. 106	80. 9	671	072	. 692
76. 0	1. 38444	1. 38835	105. 294	81. 0	1. 41737	1. 42138	114. 888
76. 1	510	902	. 482	81. 1	804	205	115. 084
76. 2	575	967	. 670	81. 2	871	272	. 280
76. 3	640	1. 39032	. 859	81. 3	938	339	. 477
76. 4	705	097	106. 047	81. 4	1. 42005	906	. 673
76. 5	770	162	. 236	81. 5	072	474	. 870
76. 6	835	228	. 424	81. 6	139	541	116. 067
76. 7	900	293	. 613	81. 7	206	608	. 264
76. 8	965	358	. 802	81. 8	273	675	. 461
76. 9	1. 39030	423	. 991	81. 9	340	742	. 658
77. 0	1. 39096	1. 39489	107. 181	82. 0	1. 42407	1. 42810	116. 856
77. 1	161	554	. 370	82. 1	475	878	117. 053
77. 2	225	619	. 560	82. 2	543	946	. 252
77. 3	291	685	. 750	82. 3	610	1. 43013	. 449
77. 4	356	750	. 940	82. 4	677	080	. 647
77. 5	422	816	108. 130	82. 5	744	148	. 845
77. 6	488	882	. 320	82. 6	811	214	118. 044
77. 7	554	949	. 511	82. 7	878	282	. 243
77. 8	619	1. 40014	. 701	82. 8	946	350	. 442
77. 9	685	080	. 892	82. 9	1. 43013	417	. 641
78. 0	1. 39751	1. 40146	109. 084	83. 0	1. 43081	1. 43486	118. 840
78. 1	816	211	. 274	83. 1	148	553	119. 039
78. 2	882	277	. 466	83. 2	216	621	. 239
78. 3	948	344	. 657	83. 3	283	688	. 438
78. 4	1. 40013	409	. 848	83. 4	351	756	. 638
78. 5	079	475	110. 041	83. 5	419	824	. 838
78. 6	145	541	. 232	83. 6	488	894	120. 039
78. 7	211	607	. 425	83. 7	555	961	. 238
78. 8	277	674	. 617	83. 8	623	1. 44029	. 439
78. 9	343	740	. 809	83. 9	691	097	. 640

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
84. 0	1. 43758	1. 44165	120. 841	89. 0	1. 47199	1. 47616	131. 096
. 1	. 43826	. 44234	121. 042	. 1	. 47269	. 47686	. 305
. 2	. 43894	. 44302	. 243	. 2	. 47339	. 47756	. 515
. 3	. 43962	. 44370	. 444	. 3	. 47409	. 47826	. 725
. 4	1. 44030	. 44438	. 646	. 4	. 47479	. 47897	. 935
. 5	. 44098	. 44507	. 847	. 5	. 47548	. 47967	132. 145
. 6	. 44166	. 44575	122. 049	. 6	. 47618	1. 48037	. 355
. 7	. 44234	. 44643	. 251	. 7	. 47688	. 48107	. 565
. 8	. 44303	. 44712	. 453	. 8	. 47758	. 48177	. 776
. 9	. 44371	. 44780	. 655	. 9	. 47828	. 48247	. 987
85. 0	1. 44439	1. 44848	122. 858	90. 0	1. 47898	1. 48317	133. 198
. 1	. 44507	. 44917	123. 061	. 1	. 47968	. 48388	. 409
. 2	. 44576	. 44985	. 263	. 2	1. 48039	. 48458	. 620
. 3	. 44644	1. 45054	. 466	. 3	. 48109	. 48529	. 832
. 4	. 44712	. 45123	. 670	. 4	. 48179	. 48599	134. 043
. 5	. 44781	. 45191	. 873	. 5	. 48249	. 48669	. 255
. 6	. 44849	. 45260	124. 076	. 6	. 48320	. 48740	. 467
. 7	. 44918	. 45329	. 280	. 7	. 48390	. 48810	. 680
. 8	. 44986	. 45397	. 484	. 8	. 48460	. 48881	. 892
. 9	1. 45055	. 45466	. 688	. 9	. 48531	. 48951	135. 104
86. 0	1. 45124	1. 45535	124. 892	91. 0	1. 48601	1. 49022	135. 317
. 1	. 45192	. 45604	125. 096	. 1	. 48672	. 49093	. 530
. 2	. 45261	. 45673	. 301	. 2	. 48742	. 49164	. 743
. 3	. 45330	. 45741	. 505	. 3	. 48813	. 49234	. 956
. 4	. 45398	. 45810	. 710	. 4	. 48883	. 49305	136. 170
. 5	. 45467	. 45879	. 915	. 5	. 48954	. 49376	. 383
. 6	. 45536	. 45949	126. 121	. 6	1. 49024	. 49447	. 597
. 7	. 45605	1. 46018	. 326	. 7	. 49095	. 49518	. 811
. 8	. 45674	. 46087	. 531	. 8	. 49166	. 49588	137. 025
. 9	. 45743	. 46156	. 737	. 9	. 49236	. 49659	. 239
87. 0	1. 45812	1. 46225	126. 943	92. 0	1. 49307	1. 49730	137. 454
. 1	. 45881	. 46294	127. 149	. 1	. 49378	. 49801	. 668
. 2	. 45950	. 46364	. 355	. 2	. 49449	. 49872	. 883
. 3	1. 46019	. 46433	. 562	. 3	. 49520	. 49944	138. 098
. 4	. 46088	. 46502	. 768	. 4	. 49591	1. 50015	. 313
. 5	. 46157	. 46572	. 975	. 5	. 49662	. 50086	. 529
. 6	. 46227	. 46641	128. 182	. 6	. 49733	. 50157	. 744
. 7	. 46296	. 46710	. 389	. 7	. 49804	. 50228	. 960
. 8	. 46365	. 46780	. 596	. 8	. 49875	. 50299	139. 176
. 9	. 46434	. 46849	. 803	. 9	. 49946	. 50371	. 392
88. 0	1. 46504	1. 46919	129. 011	93. 0	1. 50017	1. 50442	139. 608
. 1	. 46573	. 46989	. 219	. 1	. 50088	. 50513	. 824
. 2	. 46643	1. 47058	. 426	. 2	. 50159	. 50585	140. 041
. 3	. 46712	. 47128	. 635	. 3	. 50230	. 50656	. 257
. 4	. 46782	. 47198	. 843	. 4	. 50302	. 50728	. 474
. 5	. 46851	. 47267	130. 051	. 5	. 50373	. 50799	. 691
. 6	. 46921	. 47337	. 260	. 6	. 50444	. 50871	. 908
. 7	. 46990	. 47407	. 468	. 7	. 50516	. 50942	141. 126
. 8	1. 47060	. 47477	. 677	. 8	. 50587	1. 51014	. 343
. 9	. 47130	. 47547	. 886	. 9	. 50659	. 51086	. 561

TABLE 114.—*Brix, apparent density, apparent specific gravity, and grams of sucrose per 100 ml of sugar solutions*—Continued

Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo	Percentage of sucrose by weight (Brix)	Apparent density at 20° C	Apparent specific gravity at 20° C/20° C	Grams of sucrose per 100 ml weight in vacuo
1	2	3	4	1	2	3	4
94. 0	1. 50730	1. 51157	141. 779	94. 6	1. 51160	1. 51588	143. 091
. 1	. 50802	. 51229	. 997	. 7	. 51231	. 51660	. 310
. 2	. 50873	. 51301	142. 216	. 8	. 51303	. 51732	. 529
. 3	. 50945	. 51372	. 434	. 9	. 51375	. 51804	. 749
. 4	1. 51016	. 51444	. 653				
. 5	. 51088	. 51516	. 872	95. 0	1. 51447	1. 51876	143. 968

TABLE 115.—*Increase in volume when sucrose is dissolved in water at 20°C (g/100 ml)*

[*Example.*—100 ml of water at 20°C is taken and 130 g of sucrose is dissolved therein. The resultant solution at 20°C has increased in volume 81.465 ml (column 4), the total volume being 100+81.465=181.465 ml]

Weight of sucrose dissolved in 100 ml of water	Resultant solution			Weight of sucrose dissolved in 100 ml of water	Resultant solution		
	Sucrose by weight (Brix)	Specific gravity 20°/4°C	Increase in volume		Sucrose by weight (Brix)	Specific gravity 20°/4°C	Increase in volume
1	2	3	4	1	2	3	4
g	%		*ml*	*g*	%		*ml*
5	4. 7699	1. 01694	3. 078	90	47. 4125	1. 21546	56. 174
10	9. 1055	1. 03446	6. 165	100	50. 0442	1. 22981	62. 483
15	13. 0635	1. 05093	9. 259	110	52. 4250	1. 24301	68. 802
20	16. 6912	1. 06645	12. 357	120	54. 5893	1. 25520	75. 130
25	20. 0283	1. 08109	15. 461				
				130	56. 5652	1. 26649	81. 465
30	23. 1083	1. 09491	18. 570	140	58. 3763	1. 27696	87. 808
35	25. 9599	1. 10799	21. 683	150	60. 0424	1. 28671	94. 157
40	28. 6075	1. 12037	24. 801	160	61. 5803	1. 29579	100. 513
45	31. 0723	1. 13212	27. 922	170	63. 0042	1. 30429	106. 873
50	33. 3726	1. 14327	31. 048				
				180	64. 3263	1. 31225	113. 239
55	35. 5243	1. 15387	34. 177	190	65. 5572	1. 31972	119. 609
60	37. 5414	1. 16396	37. 310	200	66. 7059	1. 32675	125. 984
65	39. 4361	1. 17356	40. 447	210	67. 7805	1. 33337	132. 362
70	41. 2193	1. 18273	43. 587	220	68. 7880	1. 33961	138. 744
75	42. 9004	1. 19147	46. 729				
				230	69. 7343	1. 34551	145. 129
80	44. 4881	1. 19983	49. 874	240	70. 6249	1. 35110	151. 517

TABLE 116.—*Increase in volume when sucrose is dissolved in water at 20° C (pounds avoirdupois per gallon)*

Example—One gallon of water at 20° C is taken and 5 pounds of sugar (sucrose) is dissolved therein. The resultant solution at 20° C has increased in volume 0.373 gallon (column 4), the total volume being 1+0.373=1.373 gallons.

Sucrose dissolved in 1 gal. of water	Resultant solution			Sucrose dissolved in 1 gal. of water	Resultant solution		
	Sucrose by weight (Brix)	Specific gravity, 20°/4° C	Increase in volume		Sucrose by weight (Brix)	Specific gravity, 20°/4° C	Increase in volume
1	2	3	4	1	2	3	4
lb (avdp)	*Percent*		*gal (U. S.)*	*lb (avdp)*	*Percent*		*gal (U. S.)*
0. 1	1. 1862	1. 0028	0. 007	7	45. 6606	1. 2061	0. 523
. 2	2. 3443	1. 0074	. 015	8	48. 9881	1. 2240	. 599
. 3	3. 4760	1. 0118	. 022	9	51. 9316	1. 2403	. 674
. 4	4. 5816	1. 0162	. 029	10	54. 5539	1. 2550	. 750
. 5	5. 6622	1. 0205	. 037				
. 6	6. 7186	1. 0247	. 044	11	56. 9049	1. 2684	. 826
. 7	7. 7515	1. 0289	. 052	12	59. 0246	1. 2807	. 902
. 8	8. 7619	1. 0331	. 059	13	60. 9456	1. 2920	. 978
. 9	9. 7503	1. 0371	. 067	14	62. 6945	1. 3024	1. 055
				15	64. 2935	1. 3121	1. 131
1	10. 7175	1. 0411	. 074	16	65. 7611	1. 3210	1. 207
2	19. 3602	1. 0781	. 148	17	67. 1128	1. 3292	1. 283
3	26. 4772	1. 1104	. 223	18	68. 3618	1. 3370	1. 360
4	32. 4399	1. 1387	. 297	19	69. 5194	1. 3442	1. 436
5	37. 5080	1. 1638	. 373	20	70. 5953	1. 3509	1. 513
6	41. 8688	1. 1861	. 448				

TABLE 117.—*Weight per United States gallon and weight per cubic foot of sugar (sucrose) solutions at 20° C.*

[This table is based on the density values of Plato[1] for solutions of cane sugar. The Baumé values are from the table of Bates and Bearce.[2] The weights are for brass weights, density 8.4. One United States gallon, 231 cubic inches. One pound (avoirdupois) 453.5924 g. One United States gallon of water weighs 3,778.649 g (8.33049 pounds avoirdupois) in vacuo]

Sucrose by weight (Brix)	Weight per gallon in air [3]		Weight per gallon in vacuo [3]		Weight per cubic foot in air [3]	Specific gravity, 20°/4° C	Specific gravity, 20°/20° C	Baumé
	lb	*g*	*lb*	*g*	*lb*			
0	8. 322	3774. 6	8. 330	3778. 6	62. 25	0. 99823	1. 00000	0. 00
1	8. 354	3789. 3	8. 363	3793. 3	62. 49	1. 00212	1. 00389	. 56
2	8. 387	3804. 1	8. 395	3808. 1	62. 74	1. 00602	1. 00779	1. 12
3	8. 419	3818. 9	8. 428	3822. 9	62. 98	1. 00993	1. 01172	1. 68
4	8. 452	3833. 9	8. 461	3837. 9	63. 23	1. 01388	1. 01567	2. 24
5	8. 485	3848. 9	8. 494	3852. 9	63. 48	1. 01785	1. 01965	2. 79
6	8. 519	3864. 1	8. 528	3868. 1	63. 73	1. 02186	1. 02366	3. 35
7	8. 552	3879. 3	8. 561	3883. 3	63. 98	1. 02588	1. 02770	3. 91
8	8. 586	3894. 7	8. 595	3898. 7	64. 23	1. 02994	1. 03176	4. 46
9	8. 620	3910. 2	8. 629	3914. 2	64. 49	1. 03403	1. 03586	5. 02
10	8. 655	3925. 7	8. 664	3929. 7	64. 74	1. 03814	1. 03998	5. 57
11	8. 689	3941. 4	8. 698	3945. 4	65. 00	1. 04229	1. 04415	6. 13
12	8. 724	3957. 2	8. 733	3961. 2	65. 26	1. 04646	1. 04831	6. 68
13	8. 759	3973. 1	8. 768	3977. 1	65. 52	1. 05066	1. 05252	7. 24
14	8. 795	3989. 2	8. 803	3993. 2	65. 79	1. 05490	1. 05677	7. 79
15	8. 830	4005. 3	8. 839	4009. 3	66. 05	1. 05916	1. 06104	8. 34
16	8. 866	4021. 6	8. 875	4025. 5	66. 32	1. 06346	1. 06534	8. 89
17	8. 902	4038. 0	8. 911	4041. 9	66. 59	1. 06779	1. 06968	9. 45
18	8. 939	4054. 5	8. 947	4058. 4	66. 87	1. 07215	1. 07404	10. 00
19	8. 975	4071. 1	8. 984	4075. 0	67. 14	1. 07654	1. 07844	10. 55
20	9. 012	4087. 8	9. 021	4091. 8	67. 42	1. 08096	1. 08287	11. 10
21	9. 049	4104. 7	9. 058	4108. 6	67. 69	1. 08541	1. 08733	11. 65
22	9. 087	4121. 7	9. 095	4125. 6	67. 97	1. 08990	1. 09183	12. 20
23	9. 125	4138. 8	9. 133	4142. 8	68. 26	1. 09442	1. 09636	12. 74
24	9. 163	4156. 0	9. 171	4160. 0	68. 54	1. 09897	1. 10092	13. 29
25	9. 201	4173. 4	9. 209	4177. 3	68. 83	1. 10356	1. 10551	13. 84
26	9. 239	4190. 9	9. 248	4194. 8	69. 11	1. 10818	1. 11014	14. 39
27	9. 278	4208. 5	9. 287	4212. 4	69. 41	1. 11283	1. 11480	14. 93
28	9. 317	4226. 2	9. 326	4230. 2	69. 70	1. 11751	1. 11949	15. 48
29	9. 357	4244. 1	9. 365	4248. 0	69. 99	1. 12223	1. 12422	16. 02
30	9. 396	4262. 1	9. 405	4266. 0	70. 29	1. 12698	1. 12898	16. 57
31	9. 436	4280. 2	9. 445	4284. 2	70. 59	1. 13177	1. 13378	17. 11
32	9. 477	4298. 5	9. 485	4202. 4	70. 89	1. 13660	1. 13861	17. 65
33	9. 517	4316. 8	9. 526	4320. 8	71. 19	1. 14145	1. 14347	18. 19
34	9. 558	4335. 4	9. 566	4339. 3	71. 50	1. 14634	1. 14837	18. 73
35	9. 599	4354. 0	9. 608	4358. 0	71. 81	1. 15128	1. 15331	19. 28

[1] Wiss. Kaiserlichen Normal-Aichungs-Kommission 2, 153 (1900).
[2] Tech. Pap. BS T115 (1918).
[3] After the computations were completed, the tabulations were made by rounding off the results to the last figure given.

TABLE 117.—*Weight per United States gallon and weight per cubic foot of sugar (sucrose) solutions at 20° C*—Continued

Sucrose by weight (Brix)	Weight per gallon in air		Weight per gallon in vacuo		Weight per cubic foot in air	Specific gravity, 20°/4° C	Specific gravity, 20°/20° C	Baumé
	lb	*g*	*lb*	*g*	*lb*			
36	9. 640	4372. 8	9. 649	4376. 7	72. 12	1. 15624	1. 15828	19. 81
37	9. 682	4391. 8	9. 691	4395. 7	72. 43	1. 16124	1. 16329	20. 35
38	9. 724	4410. 8	9. 733	4414. 7	72. 74	1. 16627	1. 16833	20. 89
39	9. 766	4430. 0	9. 775	4433. 9	73. 06	1. 17134	1. 17341	21. 43
40	9. 809	4449. 3	9. 818	4453. 3	73. 38	1. 17645	1. 17853	21. 97
41	9. 852	4468. 8	9. 861	4472. 7	73. 70	1. 18159	1. 18368	22. 50
42	9. 895	4488. 4	9. 904	4492. 3	74. 02	1. 18677	1. 18887	23. 04
43	9. 939	4508. 2	9. 947	4512. 1	74. 35	1. 19199	1. 19410	23. 57
44	9. 983	4528. 1	9. 991	4532. 0	74. 68	1. 19725	1. 19936	24. 10
45	10. 027	4548. 1	10. 035	4552. 0	75. 01	1. 20254	1. 20467	24. 63
46	10. 071	4568. 3	10. 080	4572. 2	75. 34	1. 20787	1. 21001	25. 17
47	10. 116	4588. 6	10. 125	4592. 5	75. 67	1. 21324	1. 21538	25. 70
48	10. 161	4609. 1	10. 170	4613. 0	76. 01	1. 21864	1. 22080	26. 23
49	10. 207	4629. 7	10. 215	4633. 6	76. 35	1. 22409	1. 22625	26. 75
50	10. 252	4650. 4	10. 261	4654. 3	76. 69	1. 22957	1. 23174	27. 28
51	10. 299	4671. 3	10. 307	4675. 2	77. 04	1. 23508	1. 23727	27. 81
52	10. 345	4692. 4	10. 353	4696. 3	77. 39	1. 24064	1. 24284	28. 33
53	10. 392	4713. 5	10. 400	4717. 4	77. 73	1. 24623	1. 24844	28. 86
54	10. 439	4734. 9	10. 447	4738. 7	78. 09	1. 25187	1. 25408	29. 38
55	10. 486	4756. 3	10. 494	4760. 2	78. 44	1. 25754	1. 25976	29. 90
56	10. 534	4777. 9	10. 542	4781. 8	78. 80	1. 26324	1. 26548	30. 42
57	10. 581	4799. 7	10. 590	4803. 5	79. 15	1. 26899	1. 27123	30. 94
58	10. 630	4821. 6	10. 638	4825. 4	79. 52	1. 27477	1. 27703	31. 46
59	10. 678	4843. 6	10. 687	4847. 5	79. 88	1. 28060	1. 28286	31. 97
60	10. 727	4865. 8	10. 736	4869. 7	80. 25	1. 28646	1. 28873	32. 49
61	10. 777	4888. 1	10. 785	4892. 0	80. 61	1. 29235	1. 29464	33. 00
62	10. 826	4910. 6	10. 835	4914. 5	80. 98	1. 29829	1. 30059	33. 51
63	10. 876	4933. 2	10. 884	4937. 1	81. 36	1. 30427	1. 30657	34. 02
64	10. 926	4956. 0	10. 935	4959. 9	81. 73	1. 31028	1. 31260	34. 53
65	10. 977	4978. 9	10. 985	4982. 8	82. 11	1. 31633	1. 31866	35. 04
66	11. 027	5002. 0	11. 036	5005. 8	82. 49	1. 32242	1. 32476	35. 55
67	11. 079	5025. 2	11. 087	5029. 0	82. 87	1. 32855	1. 33090	36. 05
68	11. 130	5048. 5	11. 139	5052. 4	83. 26	1. 33472	1. 33708	36. 55
69	11. 182	5072. 0	11. 190	5075. 9	83. 65	1. 34093	1. 34330	37. 06
70	11. 234	5095. 7	11. 242	5099. 5	84. 04	1. 34717	1. 34956	37. 56
71	11. 286	5119. 5	11. 295	5123. 3	84. 43	1. 35346	1. 35585	38. 06
72	11. 339	5143. 4	11. 348	5147. 2	84. 82	1. 35978	1. 36218	38. 55
73	11. 392	5167. 5	11. 401	5171. 3	85. 22	1. 36614	1. 36856	39. 05
74	11. 446	5191. 7	11. 454	5195. 5	85. 62	1. 37254	1. 37496	39. 54
75	11. 499	5216. 1	11. 508	5219. 9	86. 02	1. 37897	1. 38141	40. 03
76	11. 554	5240. 6	11. 562	5244. 4	86. 43	1. 38545	1. 38790	40. 53
77	11. 608	5265. 2	11. 616	5269. 0	86. 83	1. 39196	1. 39442	41. 01
78	11. 663	5290. 0	11. 671	5293. 8	87. 24	1. 39850	1. 40098	41. 50
79	11. 717	5315. 0	11. 726	5318. 8	87. 65	1. 40509	1. 40758	41. 99
80	11. 773	5340. 0	11. 781	5343. 8	88. 07	1. 41172	1. 41421	42. 47

TABLE 117.—*Weight per United States gallon and weight per cubic foot of sugar (sucrose) solutions at 20° C*—Continued

Sucrose by weight (Brix)	Weight per gallon in air		Weight per gallon in vacuo		Weight per cubic foot in air	Specific gravity, 20°/4° C	Specific gravity, 20°/20° C	Baume
	lb	*g*	*lb*	*g*	*lb*			
81	11. 828	5365. 2	11. 837	5369. 0	88. 48	1. 41837	1. 42088	42. 95
82	11. 884	5390. 6	11. 893	5394. 4	88. 90	1. 42507	1. 42759	43. 43
83	11. 940	5416. 1	11. 949	5419. 9	89. 32	1. 43181	1. 43434	43. 91
84	11. 997	5441. 7	12. 005	5445. 5	89. 74	1. 43858	1. 44112	44. 38
85	12. 054	5467. 5	12. 062	5471. 3	90. 17	1. 44539	1. 44794	44. 86
86	12. 111	5493. 4	12. 119	5497. 2	90. 60	1. 45223	1. 45480	45. 33
87	12. 168	5519. 5	12. 177	5523. 3	91. 03	1. 45911	1. 46170	45. 80
88	12. 226	5545. 6	12. 234	5549. 4	91. 46	1. 46603	1. 46862	46. 27
89	12. 284	5572. 0	12. 292	5575. 7	91. 89	1. 47299	1. 47559	46. 73
90	12. 342	5598. 4	12. 351	5602. 2	92. 33	1. 47998	1. 48259	47. 20
91	12. 401	5625. 1	12. 409	5628. 8	92. 77	1. 48700	1. 48963	47. 66
92	12. 460	5651. 8	12. 468	5655. 5	93. 21	1. 49406	1. 49671	48. 12
93	12. 519	5678. 6	12. 527	5682. 4	93. 65	1. 50116	1. 50381	48. 58
94	12. 579	5705. 7	12. 587	5709. 4	94. 10	1. 50829	1. 51096	49. 03
95	12. 639	5732. 8	12. 647	5736. 5	94. 54	1. 51546	1. 51814	49. 49

TABLE 118.—*Weight per United States gallon of sugar (sucrose) solutions at different temperatures*

[The values obtained by extrapolation are given in italics]

Sucrose by weight (Brix)	Weight per gallon in air at $t°$ C									
	$t=10°$ C		$t=15°$ C		$t=20°$ C		$t=25°$ C		$t=30°$ C	
	lb	*g*	*lb*	*g*	*lb*	*g*	*lb*	*g*	*lb*	*g*
0	8. 334	3, 780	8. 329	3, 778	8. 322	3, 775	8. 312	3, 770	8. 301	3, 765
5	8. 500	3, 856	8. 494	3, 853	8. 485	3, 849	8. 475	3, 844	8. 463	3, 839
10	8. 672	3, 933	8. 664	3, 930	8. 655	3, 926	8. 644	3, 921	8. 631	3, 915
15	8. 849	4, 014	8. 841	4, 010	8. 830	4, 005	8. 818	4, 000	8. 805	3, 994
20	9. 034	4, 098	9. 023	4, 093	9. 012	4, 088	8. 999	4, 082	8. 985	4, 075
25	9. 225	4, 184	9. 213	4, 179	9. 201	4, 173	9. 187	4, 167	9. 171	4, 160
30	9. 423	4, 274	9. 410	4, 268	9. 396	4, 262	9. 381	4, 255	9. 365	4, 248
35	9. 628	4, 367	9. 614	4, 361	9. 599	4, 354	9. 583	4, 347	9. 566	4, 339
40	9. 840	4, 464	9. 825	4, 457	9. 809	4, 449	9. 792	4, 442	9. 774	4, 433
45	10. 060	4, 563	10. 044	4, 556	10. 027	4, 548	10. 009	4, 540	9. 990	4, 531
50	10. 288	4, 667	10. 271	4, 659	10. 252	4, 650	10. 234	4, 642	10. 214	4, 633
55	10. 523	4, 773	10. 505	4, 765	10. 486	4, 756	10. 466	4, 747	10. 446	4, 738
60	10. 767	4, 884	10. 747	4, 875	10. 727	4, 866	10. 707	4, 856	10. 685	4, 847
65	11. 018	4, 998	10. 997	4, 988	10. 977	4, 979	10. 955	4, 969	10. 933	4, 959
70	11. 277	5, 115	11. 256	5, 105	11. 234	5, 096	11. 212	5, 086	11. 189	5, 075
75	*11. 544*	*5, 236*	11. 522	5, 226	11. 499	5, 216	*11. 477*	*5, 206*	*11. 453*	*5, 195*
80	*11. 818*	*5, 361*	11. 796	5, 351	11. 773	5, 340	*11. 749*	*5, 329*	*11. 725*	*5, 319*
85	*12. 101*	*5, 489*	12. 078	5, 478	12. 054	5, 467	*12. 030*	*5, 457*	*12. 005*	*5, 445*
90	*12. 391*	*5, 620*	12. 367	5, 610	12. 342	5, 598	*12. 318*	*5, 587*	*12. 293*	*5, 576*
95	*12. 688*	*5, 755*	12. 664	5, 744	12. 639	5, 733	*12. 613*	*5, 721*	*12. 587*	*5, 709*

TABLE 119.—*Volume of sucrose solutions at different temperatures*[1]

[Volume at 20°C=1.0000]

Temperature	Percentage of sucrose by weight							
	0	5	10	15	20	25	30	35
	"*f*", VOLUME FACTOR (VOLUME *t*=VOLUME 20°C×*f*)							
°*C*								
0	0. 9984	0. 9976	0. 9969	0. 9964	0. 9958	0. 9954	0. 9949	0. 9945
5	. 9982	. 9978	. 9974	. 9970	. 9966	. 9963	. 9960	. 9957
10	. 9985	. 9983	. 9981	. 9978	. 9976	. 9974	. 9972	. 9970
15	. 9991	. 9990	. 9989	. 9988	. 9987	. 9986	. 9985	. 9984
20	1. 0000	1. 0000	1. 0000	1. 0000	1. 0000	1. 0000	1. 0000	1. 0000
25	1. 0012	1. 0012	1. 0013	1. 0014	1. 0014	1. 0015	1. 0016	1. 0017
30	1. 0026	1. 0026	1. 0027	1. 0029	1. 0030	1. 0032	1. 0033	1. 0035
35	1. 0042	1. 0043	1. 0044	1. 0046	1. 0048	1. 0050	1. 0052	1. 0054
40	1. 0060	1. 0061	1. 0063	1. 0065	1. 0068	1. 0070	1. 0072	1. 0074
45	1. 0080	1. 0081	1. 0084	1. 0086	1. 0089	1. 0091	1. 0094	1. 0096
50	1. 0102	1. 0104	1. 0106	1. 0109	1. 0112	1. 0115	1. 0117	1. 0119
55	1. 0126	1. 0128	1. 0131	1. 0134	1. 0137	1. 0139	1. 0141	1. 0143
60	1. 0152	1. 0155	1. 0158	1. 0161	1. 0163	1. 0165	1. 0167	1. 0168
65	1. 0179	1. 0184	1. 0186	1. 0189	1. 0191	1. 0194	1. 0196	1. 0196
70	1. 0209	1. 0213	1. 0215	1. 0218	1. 0218	1. 0221	1. 0223	1. 0224
75	1. 0241	1. 0243	1. 0244	1. 0247	1. 0248	1. 0250	1. 0251	1. 0252
80	1. 0274	1. 0273	1. 0275	1. 0277	1. 0279	1. 0280	1. 0281	1. 0281
85	1. 0308	1. 0307	1. 0309	1. 0309	1. 0312	1. 0312	1. 0312	1. 0312
90	1. 0342	1. 0342	1. 0344	1. 0344	1. 0347	1. 0346	1. 0345	1. 0344
95	1. 0376	1. 0379	1. 0380	1. 0380	1. 0382	1. 0381	1. 0379	1. 0377
100	1. 0411	1. 0417	1. 0418	1. 0417	1. 0417	1. 0415	1. 0413	1. 0412

[1] Factors for concentrations from 0 to 70 percent at temperatures from 0° to 60°C computed from Plato's density tables (Kaiserlichen Normal-Eichungs-Kommission, Wiss. Abh. 2 (1900)); remaining factors computed from Th. Gerlach, Z. Ver. deut. Zucker-Ind. **13**, 320 (1863).

TABLE 119.—*Volume of sucrose solutions at different temperatures* [1]—Continued

[Volume at 20°C=1.0000]

Temperature	Percentage of sucrose by weight							
	40	45	50	55	60	65	70	75
	"*f*", VOLUME FACTOR (VOLUME *t*=VOLUME 20°C×*f*)							
°*C*								
0	0. 9941	0. 9937	0. 9934	0. 9931	0. 9929	0. 9928	0. 9926	0. 9927
5	. 9954	. 9952	. 9949	. 9948	. 9946	. 9945	. 9944	. 9945
10	. 9969	. 9967	. 9966	. 9964	. 9963	. 9963	. 9962	. 9964
15	. 9984	. 9983	. 9982	. 9982	. 9981	. 9981	. 9981	. 9982
20	1. 0000	1. 0000	1. 0000	1. 0000	1. 0000	1. 0000	1. 0000	1. 0000
25	1. 0018	1. 0018	1. 0018	1. 0019	1. 0019	1. 0019	1. 0020	1. 0019
30	1. 0036	1. 0037	1. 0038	1. 0039	1. 0039	1. 0039	1. 0040	1. 0038
35	1. 0056	1. 0057	1. 0058	1. 0059	1. 0060	1. 0060	1. 0061	1. 0058
40	1. 0076	1. 0078	1. 0079	1. 0080	1. 0081	1. 0081	1. 0082	1. 0078
45	1. 0098	1. 0099	1. 0100	1. 0102	1. 0102	1. 0103	1. 0103	1. 0099
50	1. 0120	1. 0122	1. 0123	1. 0124	1. 0125	1. 0125	1. 0125	1. 0121
55	1. 0144	1. 0145	1. 0147	1. 0148	1. 0148	1. 0148	1. 0148	1. 0143
60	1. 0169	1. 0170	1. 0171	1. 0172	1. 0172	1. 0172	1. 0171	1. 0166
65	1. 0200	1. 0202	1. 0199	1. 0199	1. 0198	1. 0194	1. 0189	1. 0190
70	1. 0227	1. 0229	1. 0225	1. 0225	1. 0223	1. 0219	1. 0215	1. 0214
75	1. 0254	1. 0257	1. 0252	1. 0251	1. 0250	1. 0244	1. 0241	1. 0238
80	1. 0283	1. 0286	1. 0280	1. 0278	1. 0277	1. 0270	1. 0268	1. 0263
85	1. 0312	1. 0317	1. 0310	1. 0306	1. 0305	1. 0297	1. 0294	1. 0289
90	1. 0343	1. 0347	1. 0340	1. 0334	1. 0334	1. 0326	1. 0322	1. 0316
95	1. 0375	1. 0378	1. 0371	1. 0364	1. 0363	1. 0354	1. 0351	1. 0343
100	1. 0409	1. 0409	1 0403	1. 0395	1. 0393	1. 0383	1. 0380	1. 0370

[1] Factors for concentrations from 0 to 70 percent at temperatures from 0° to 60°C computed from Plato's density tables (Kaiserlichen Normal-Eichungs-Kommission, Wiss. Abh. 2 (1900)); remaining factors computed from Th. Gerlach, Z. Ver. deut. Zucker-Ind. **13**, 320 (1863).

TABLE 120.—*Density of levulose solutions and mean density and expansion coefficients between 20° and 25° C*

[All weights corrected to vacuum]

Levulose by weight	D_4^{20}	D_4^{25}	$-\Delta D/\Delta t$	$\Delta v/\Delta t$
%			$\times 10^{-6}$	$\times 10^{-6}$
0	0. 99823	0. 99708	231	231
1	1. 00214	1. 00095	238	237
2	1. 00607	1. 00484	245	243
3	1. 01003	1. 00877	252	249
4	1. 01402	1. 01272	259	255
5	1. 01803	1. 01670	266	261
6	1. 02207	1. 02071	273	267
7	1. 02614	1. 02475	280	273
8	1. 03024	1. 02881	287	278
9	1. 03437	1. 03290	294	284
10	1. 03853	1. 03702	301	290
11	1. 04271	1. 04118	308	295
12	1. 04692	1. 04535	315	300
13	1. 05116	1. 04955	323	307
14	1. 05543	1. 05378	330	313
15	1. 05972	1. 05804	337	318
16	1. 06405	1. 06233	345	324
17	1. 06840	1. 06664	352	329
18	1. 07278	1. 07098	360	336
19	1. 07719	1. 07535	367	341
20	1. 08162	1. 07975	375	347
			$\times 10^{-5}$	$\times 10^{-5}$
21	1. 08606	1. 0842	38	35
22	1. 09055	1. 0886	38	35
23	1. 09507	1. 0931	39	36
24	1. 09962	1. 0976	40	36
25	1. 10420	1. 1022	41	37
26	1. 1088	1. 10675	41	37
27	1. 11345	1. 11135	42	38
28	1. 1181	1. 1160	43	38
29	1. 1229	1. 1207	43	39
30	1. 1276	1. 1254	44	39
31	1. 1324	1. 13015	45	40
32	1. 1372	1. 1349	46	40
33	1. 14205	1. 1397	46	40
34	1. 1469	1. 1446	47	41
35	1. 15185	1. 1495	48	41
36	1. 1568	1. 1544	48	42
37	1. 1618	1. 1593	49	42
38	1. 1668	1. 1643	50	43
39	1. 1718	1. 1693	50	43
40	1. 1769	1. 17435	51	43

TABLE 120.—*Density of levulose solutions and mean density and expansion coefficients between 20° and 25° C*—Continued

Levulose by weight	D_4^{20}	D_4^{25}	$-\Delta D/\Delta t$ $\times 10^{-5}$	$\Delta v/\Delta t$ $\times 10^{-5}$
41	1. 1820	1. 1794	52	44
42	1. 1872	1. 1845	53	44
43	1. 1923	1. 1897	53	45
44	1. 1975	1. 19485	54	45
45	1. 2028	1. 20005	55	45
46	1. 20805	1. 2053	55	46
47	1. 2134	1. 2106	56	46
48	1. 2187	1. 2159	57	46
49	1. 2241	1. 2212	57	47
50	1. 2295	1. 2266	58	47
51	1. 2349	1. 2320	59	47
52	1. 2404	1. 2374	59	48
53	1. 2459	1. 2429	60	48
54	1. 2514	1. 2484	60	48
55	1. 2570	1. 2539	61	49
56	1. 2626	1. 2595	62	49
57	1. 2682	1. 2651	62	49
58	1. 2739	1. 2707	63	50
59	1. 2796	1. 2764	64	50
60	1. 2853	1. 2821	64	50
61	1. 2911	1. 2878	65	50
62	1. 2969	1. 2936	66	51
63	1. 3027	1. 2994	66	51
64	1. 3086	1. 3052	67	51
65	1. 3145	1. 3111	67	51
66	1. 3204	1. 3170	68	51
67	1. 3263	1. 3229	69	52
68	1. 3323	1. 3289	69	52
69	1. 3384	1. 3349	70	52
70	1. 3444	1. 3409	70	52
71	1. 3505	1. 3470	71	53

TABLE 121.—*Density of dextrose solutions* [1]

$[D_4^{20}=0.99840+0.003788p+0.00001412p^2]$

Concentration by weight in vacuo	D_4^{20}	Concentration by weight in vacuo	D_4^{20}	Concentration by weight in vacuo	D_4^{20}
Percent		*Percent*		*Percent*	
4	1. 01378	13	1. 05003	22	1. 08857
5	1. 01769	14	1. 05420	23	1. 09299
6	1. 02164	15	1. 05840	24	1. 09744
7	1. 02561	16	1. 06262	25	1. 10192
8	1. 02961	17	1. 06688	26	1. 10643
9	1. 03364	18	1. 07116	27	1. 11097
10	1. 03769	19	1. 07547	28	1. 11553
11	1. 04178	20	1. 07981	29	1. 12013
12	1. 04589	21	1. 08417	30	1. 12475

[1] R. F. Jackson, Bul. BS **13**, 642 (1916) S293.

TABLE 122.—*Refractive index of sucrose solutions at 20° C* [1]

Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}
%		%		%		%	
0. 0	1. 33299	3. 0	1. 33733	6. 0	1. 34176	9. 0	1. 34629
. 1	1. 33313	. 1	1. 33748	. 1	1. 34191	. 1	1. 34644
. 2	1. 33328	. 2	1. 33762	. 2	1. 34206	. 2	1. 34660
. 3	1. 33342	. 3	1. 33777	. 3	1. 34221	. 3	1. 34675
. 4	1. 33357	. 4	1. 33792	. 4	1. 34236	. 4	1. 34691
. 5	1. 33371	. 5	1. 33807	. 5	1. 34251	. 5	1. 34706
. 6	1. 33385	. 6	1. 33821	. 6	1. 34266	. 6	1. 34721
. 7	1. 33400	. 7	1. 33836	. 7	1. 34281	. 7	1. 34537
. 8	1. 33414	. 8	1. 33851	. 8	1. 34296	. 8	1. 34752
. 9	1. 33429	. 9	1. 33865	. 9	1. 34311	. 9	1. 34768
1. 0	1. 33443	4. 0	1. 33880	7. 0	1. 34326	10. 0	1. 34783
. 1	1. 33457	. 1	1. 33895	. 1	1. 34341	. 1	1. 34798
. 2	1. 33472	. 2	1. 33909	. 2	1. 34356	. 2	1. 34814
. 3	1. 33487	. 3	1. 33924	. 3	1. 34371	. 3	1. 34829
. 4	1. 33501	. 4	1. 33939	. 4	1. 34386	. 4	1. 34845
. 5	1. 33515	. 5	1. 33953	. 5	1. 34401	. 5	1. 34860
. 6	1. 33530	. 6	1. 33968	. 6	1. 34417	. 6	1. 34875
. 7	1. 33545	. 7	1. 33983	. 7	1. 34432	. 7	1. 34891
. 8	1. 33559	. 8	1. 33998	. 8	1. 34447	. 8	1. 34906
. 9	1. 33573	. 9	1. 34012	. 9	1. 34462	. 9	1. 34922
2. 0	1. 33588	5. 0	1. 34027	8. 0	1. 34477	11. 0	1. 34937
. 1	1. 33603	. 1	1 34042	. 1	1. 34492	. 1	1. 34953
. 2	1. 33617	. 2	1. 34057	. 2	1. 34507	. 2	1. 34968
. 3	1. 33631	. 3	1. 34072	. 3	1. 34523	. 3	1. 34984
. 4	1. 33646	. 4	1. 34087	. 4	1. 34538	. 4	1. 34999
. 5	1. 33661	. 5	1. 34101	. 5	1. 34553	. 5	1. 35015
. 6	1. 33675	. 6	1. 34116	. 6	1. 34568	. 6	1. 35031
. 7	1. 33689	. 7	1. 34131	. 7	1 34583	. 7	1. 35046
. 8	1. 33704	. 8	1. 34146	. 8	1. 34599	. 8	1. 35062
. 9	1. 33719	. 9	1. 34161	. 9	1. 34614	. 9	1. 35077

[1] The values of refractive indices for whole percents of sucrose are those of the "International Scale of Refractive Indices of Sucrose at 20° C, 1936", adopted by the International Commission for Uniform Methods of Sugar Analysis, Ninth Session, London, 1936. The remaining values were obtained by interpolation. Int. Sugar J. **39**, 22s (1937).

TABLE 122.—*Refractive index of sucrose solutions at 20° C*—Continued

Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}
%		%		%		%	
12. 0	1. 35093	17. 0	1. 35890	22. 0	1. 36719	27. 0	1. 3758
. 1	1. 35109	. 1	1. 35906	. 1	1. 36736	. 1	1. 3760
. 2	1. 35124	. 2	1. 35923	. 2	1. 36753	. 2	1. 3761
. 3	1. 35140	. 3	1. 35939	. 3	1. 36770	. 3	1. 3763
. 4	1. 35156	. 4	1. 35955	. 4	1. 36787	. 4	1. 3765
. 5	1. 35171	. 5	1. 35971	. 5	1. 36803	. 5	1. 3767
. 6	1. 35187	. 6	1. 35988	. 6	1. 36820	. 6	1. 3768
. 7	1. 35203	. 7	1. 36004	. 7	1. 36837	. 7	1. 3770
. 8	1. 35219	. 8	1. 36020	. 8	1. 36854	. 8	1. 3772
. 9	1. 35234	. 9	1. 36037	. 9	1. 36871	. 9	1. 3773
13. 0	1. 35250	18. 0	1. 36053	23. 0	1. 36888	28. 0	1. 3775
. 1	1. 35266	. 1	1. 36069	. 1	1. 36905	. 1	1. 3777
. 2	1. 35282	. 2	1. 36086	. 2	1. 36922	. 2	1. 3779
. 3	1. 35297	. 3	1. 36103	. 3	1. 36939	. 3	1. 3780
. 4	1. 35313	. 4	1. 36119	. 4	1. 36956	. 4	1. 3782
. 5	1. 35329	. 5	1. 36135	. 5	1. 36973	. 5	1. 3784
. 6	1. 35345	. 6	1. 36152	. 6	1. 36991	. 6	1. 3786
. 7	1. 35361	. 7	1. 36169	. 7	1. 37008	. 7	1. 3788
. 8	1. 35376	. 8	1. 36185	. 8	1. 37025	. 8	1. 3789
. 9	1. 35392	. 9	1. 36201	. 9	1. 37042	. 9	1. 3791
14. 0	1. 35408	19. 0	1. 36218	24. 0	1. 37059	29. 0	1. 3793
. 1	1. 35424	. 1	1. 36235	. 1	1. 3708	. 1	1. 3795
. 2	1. 35440	. 2	1. 36251	. 2	1. 3709	. 2	1. 3797
. 3	1. 35456	. 3	1. 36268	. 3	1. 3711	. 3	1. 3798
. 4	1. 35472	. 4	1. 36284	. 4	1. 3713	. 4	1. 3800
. 5	1. 35487	. 5	1. 36301	. 5	1. 3715	. 5	1. 3802
. 6	1. 35503	. 6	1. 36318	. 6	1. 3716	. 6	1. 3804
. 7	1. 35519	. 7	1. 36334	. 7	1. 3718	. 7	1. 3806
. 8	1. 35535	. 8	1. 36351	. 8	1. 3720	. 8	1. 3807
. 9	1. 35551	. 9	1. 36367	. 9	1. 3721	. 9	1. 3809
15. 0	1. 35567	20. 0	1. 36384	25. 0	1. 3723	30. 0	1. 3811
. 1	1. 35583	. 1	1. 36401	. 1	1. 3725	. 1	1. 3813
. 2	1. 35599	. 2	1. 36417	. 2	1. 3726	. 2	1. 3815
. 3	1. 35615	. 3	1. 36434	. 3	1. 3728	. 3	1. 3816
. 4	1. 35631	. 4	1. 36451	. 4	1. 3730	. 4	1. 3818
. 5	1. 35647	. 5	1. 36467	. 5	1. 3731	. 5	1. 3820
. 6	1. 35664	. 6	1. 36484	. 6	1. 3733	. 6	1. 3822
. 7	1. 35680	. 7	1. 36501	. 7	1. 3735	. 7	1. 3824
. 8	1. 35696	. 8	1. 36518	. 8	1. 3737	. 8	1. 3825
. 9	1. 35712	. 9	1. 36534	. 9	1. 3738	. 9	1. 3827
16. 0	1. 35728	21. 0	1. 36551	26. 0	1. 3740	31. 0	1. 3829
. 1	1. 35744	. 1	1. 36568	. 1	1. 3742	. 1	1. 3831
. 2	1. 35760	. 2	1. 36585	. 2	1. 3744	. 2	1. 3833
. 3	1. 35777	. 3	1. 36601	. 3	1. 3745	. 3	1. 3834
. 4	1. 35793	. 4	1. 36618	. 4	1. 3747	. 4	1. 3836
. 5	1. 35809	. 5	1. 36635	. 5	1. 3749	. 5	1. 3838
. 6	1. 35825	. 6	1. 36652	. 6	1. 3751	. 6	1. 3840
. 7	1. 35841	. 7	1. 36669	. 7	1. 3753	. 7	1. 3842
. 8	1. 35858	. 8	1. 36685	. 8	1. 3754	. 8	1. 3843
. 9	1. 35874	. 9	1. 36702	. 9	1. 3756	. 9	1. 3845

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TABLE 122.—*Refractive index of sucrose solutions at 20° C*—Continued

Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}
%		%		%		%	
32. 9	1. 3847	37. 0	1. 3939	42. 0	1. 4036	47. 0	1. 4137
. 1	1. 3849	. 1	1. 3941	. 1	1. 4038	. 1	1. 4139
. 2	1. 3851	. 2	1. 3943	. 2	1. 4040	. 2	1. 4141
. 3	1. 3852	. 3	1. 3945	. 3	1. 4042	. 3	1. 4143
. 4	1. 3854	. 4	1. 3947	. 4	1. 4044	. 4	1. 4145
. 5	1. 3856	. 5	1. 3949	. 5	1. 4046	. 5	1. 4147
. 6	1. 3858	. 6	1. 3950	. 6	1. 4048	. 6	1. 4150
. 7	1. 3860	. 7	1. 3952	. 7	1. 4050	. 7	1. 4152
. 8	1. 3861	. 8	1. 3954	. 8	1. 4052	. 8	1. 4154
. 9	1. 3863	. 9	1. 3956	. 9	1. 4054	. 9	1. 4156
33. 0	1. 3865	38. 0	1. 3958	43. 0	1. 4056	48. 0	1. 4158
. 1	1. 3867	. 1	1. 3960	. 1	1. 4058	. 1	1. 4160
. 2	1. 3869	. 2	1. 3962	. 2	1. 4060	. 2	1. 4162
. 3	1. 3870	. 3	1. 3964	. 3	1. 4062	. 3	1. 4164
. 4	1. 3872	. 4	1. 3966	. 4	1. 4064	. 4	1. 4166
. 5	1. 3874	. 5	1. 3968	. 5	1. 4066	. 5	1. 4169
. 6	1. 3876	. 6	1. 3970	. 6	1. 4068	. 6	1. 4171
. 7	1. 3878	. 7	1. 3972	. 7	1. 4070	. 7	1. 4173
. 8	1. 3879	. 8	1. 3974	. 8	1. 4072	. 8	1. 4175
. 9	1. 3881	. 9	1. 3976	. 9	1. 4074	. 9	1. 4177
34. 0	1. 3883	39. 0	1. 3978	44. 0	1. 4076	49. 0	1. 4179
. 1	1. 3885	. 1	1. 3980	. 1	1. 4078	. 1	1. 4181
. 2	1. 3887	. 2	1. 3982	. 2	1. 4080	. 2	1. 4183
. 3	1. 3889	. 3	1. 3984	. 3	1. 4082	. 3	1. 4185
. 4	1. 3891	. 4	1. 3986	. 4	1. 4084	. 4	1. 4187
. 5	1. 3893	. 5	1. 3987	. 5	1. 4086	. 5	1. 4189
. 6	1. 3894	. 6	1. 3989	. 6	1. 4088	. 6	1. 4192
. 7	1. 3896	. 7	1. 3991	. 7	1. 4090	. 7	1. 4194
. 8	1. 3898	. 8	1. 3993	. 8	1. 4092	. 8	1. 4196
. 9	1. 3900	. 9	1. 3995	. 9	1. 4094	. 9	1. 4198
35. 0	1. 3902	40. 0	1. 3997	45. 0	1. 4096	50. 0	1. 4200
. 1	1. 3904	. 1	1. 3999	. 1	1. 4098	. 1	1. 4202
. 2	1. 3906	. 2	1. 4001	. 2	1. 4100	. 2	1. 4204
. 3	1. 3907	. 3	1. 4003	. 3	1. 4102	. 3	1. 4206
. 4	1. 3909	. 4	1. 4005	. 4	1. 4104	. 4	1. 4208
. 5	1. 3911	. 5	1. 4007	. 5	1. 4107	. 5	1. 4211
. 6	1. 3913	. 6	1. 4008	. 6	1. 4109	. 6	1. 4213
. 7	1. 3915	. 7	1. 4010	. 7	1. 4111	. 7	1. 4215
. 8	1. 3916	. 8	1. 4012	. 8	1. 4113	. 8	1. 4217
. 9	1. 3918	. 9	1. 4014	. 9	1. 4115	. 9	1. 4219
36. 0	1. 3920	41. 0	1. 4016	46. 0	1. 4117	51. 0	1. 4221
. 1	1. 3922	. 1	1. 4018	. 1	1. 4119	. 1	1. 4223
. 2	1. 3924	. 2	1. 4020	. 2	1. 4121	. 2	1. 4225
. 3	1. 3926	. 3	1. 4022	. 3	1. 4123	. 3	1. 4227
. 4	1. 3928	. 4	1. 4024	. 4	1. 4125	. 4	1. 4229
. 5	1. 3929	. 5	1. 4026	. 5	1. 4127	. 5	1. 4231
. 6	1. 3931	. 6	1. 4028	. 6	1. 4129	. 6	1. 4234
. 7	1. 3933	. 7	1. 4030	. 7	1. 4131	. 7	1. 4236
. 8	1. 3935	. 8	1. 4032	. 8	1. 4133	. 8	1. 4238
. 9	1. 3937	. 9	1. 4034	. 9	1. 4135	. 9	1. 4240

TABLE 122.—*Refractive index of sucrose solutions at 20° C*—Continued

Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}
%		%		%		%	
52. 0	1. 4242	57. 0	1. 4351	62.0	1. 4464	67.0	1. 4579
. 1	1. 4244	. 1	1. 4353	.1	1. 4466	.1	1. 4581
. 2	1. 4246	. 2	1. 4355	.2	1. 4468	.2	1. 4584
. 3	1. 4249	. 3	1. 4358	.3	1. 4471	.3	1. 4586
. 4	1. 4251	. 4	1. 4360	.4	1. 4473	.4	1. 4589
. 5	1. 4253	. 5	1. 4362	.5	1. 4475	.5	1. 4591
. 6	1. 4255	. 6	1. 4364	.6	1. 4477	.6	1. 4593
. 7	1. 4257	. 7	1. 4366	.7	1. 4479	.7	1. 4596
. 8	1. 4260	. 8	1. 4369	.8	1. 4482	.8	1. 4598
. 9	1. 4262	. 9	1. 4371	.9	1. 4484	.9	1. 4601
53. 0	1. 4264	58. 0	1. 4373	63.0	1. 4486	68.0	1. 4603
. 1	1. 4266	. 1	1. 4375	.1	1. 4488	.1	1. 4605
. 2	1. 4268	. 2	1. 4378	.2	1. 4491	.2	1. 4608
. 3	1. 4270	. 3	1. 4380	.3	1. 4493	.3	1. 4610
. 4	1. 4272	. 4	1. 4382	.4	1. 4495	.4	1. 4613
. 5	1. 4275	. 5	1. 4385	.5	1. 4497	.5	1. 4615
. 6	1. 4277	. 6	1. 4387	.6	1. 4500	.6	1. 4617
. 7	1. 4279	. 7	1. 4389	.7	1. 4502	.7	1. 4620
. 8	1. 4281	. 8	1. 4391	.8	1. 4504	.8	1. 4622
. 9	1. 4283	. 9	1. 4394	.9	1. 4507	.9	1. 4625
54. 0	1. 4285	59. 0	1. 4396	64.0	1. 4509	69.0	1. 4627
. 1	1. 4287	. 1	1. 4398	.1	1. 4511	.1	1. 4629
. 2	1. 4289	. 2	1. 4400	.2	1. 4514	.2	1. 4632
. 3	1. 4292	. 3	1. 4403	.3	1. 4516	.3	1 4634
. 4	1. 4294	. 4	1. 4405	.4	1. 4518	.4	1. 4637
. 5	1. 4296	. 5	1. 4407	.5	1. 4521	.5	1. 4639
. 6	1. 4298	. 6	1. 4409	.6	1. 4523	.6	1. 4641
. 7	1. 4300	. 7	1. 4411	.7	1. 4525	.7	1. 4644
. 8	1. 4303	. 8	1. 4414	.8	1. 4527	.8	1. 4646
. 9	1. 4305	. 9	1. 4416	.9	1. 4530	.9	1. 4649
55. 0	1. 4307	60.0	1. 4418	65.0	1. 4532	70.0	1. 4651
. 1	1. 4309	.1	1. 4420	.1	1. 4534	.1	1. 4653
. 2	1. 4311	.2	1. 4423	.2	1. 4537	.2	1. 4656
. 3	1. 4313	.3	1. 4425	.3	1. 4539	.3	1. 4658
. 4	1. 4316	.4	1. 4427	.4	1. 4541	.4	1. 4661
. 5	1. 4318	.5	1. 4429	.5	1. 4544	.5	1. 4663
. 6	1. 4320	.6	1. 4432	.6	1. 4546	.6	1. 4666
. 7	1. 4322	.7	1. 4434	.7	1. 4548	.7	1. 4668
. 8	1. 4325	.8	1. 4436	.8	1. 4550	.8	1. 4671
. 9	1. 4327	.9	1. 4439	.9	1. 4553	.9	1. 4673
56. 0	1. 4329	61.0	1. 4441	66.0	1. 4555	71.0	1. 4676
. 1	1. 4331	.1	1. 4443	.1	1. 4557	.1	1. 4678
. 2	1. 4333	.2	1. 4446	.2	1. 4560	.2	1. 4681
. 3	1. 4336	.3	1. 4448	.3	1. 4562	.3	1. 4683
. 4	1. 4338	.4	1. 4450	.4	1. 4565	.4	1. 4685
. 5	1. 4340	.5	1. 4453	.5	1. 4567	.5	1. 4688
. 6	1. 4342	.6	1. 4455	.6	1. 4569	.6	1. 4690
. 7	1. 4344	.7	1. 4457	.7	1. 4572	.7	1. 4693
. 8	1. 4347	.8	1. 4459	.8	1. 4574	.8	1. 4695
. 9	1. 4349	.9	1. 4462	.9	1. 4577	.9	1. 4698

TABLE 122.—*Refractive index of sucrose solutions at 20°C*—Continued

Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}	Sucrose by weight	Refractive index, n_D^{20}
%		%		%		%	
72.0	1. 4700	75.3	1. 4782	78.6	1. 4865	81.9	1. 4951
.1	1. 4703	.4	1. 4784	.7	1. 4868		
.2	1. 4705	.5	1. 4787	.8	1. 4871	82.0	1. 4954
.3	1. 4708	.6	1. 4789	.9	1. 4873	.1	1. 4956
.4	1. 4710	.7	1. 4792			.2	1. 4959
.5	1. 4713	.8	1. 4794	79.0	1. 4876	.3	1. 4962
.6	1. 4715	.9	1. 4797	.1	1. 4878	.4	1. 4964
.7	1. 4717			.2	1. 4881	.5	1. 4967
.8	1. 4720	76.0	1. 4799	.3	1. 4883	.6	1. 4970
.9	1. 4722	.1	1. 4802	.4	1. 4886	.7	1. 4972
		.2	1. 4804	.5	1. 4888	.8	1. 4975
73.0	1. 4725	.3	1. 4807	.6	1. 4891	.9	1. 4978
.1	1. 4727	.4	1. 4810	.7	1. 4893		
.2	1. 4730	.5	1. 4812	.8	1. 4896	83.0	1. 4980
.3	1. 4732	.6	1. 4815	.9	1. 4898	.1	1. 4983
.4	1. 4735	.7	1. 4817			.2	1. 4985
.5	1. 4737	.8	1. 4820	80.0	1. 4901	.3	1. 4988
.6	1. 4740	.9	1. 4822	.1	1. 4904	.4	1. 4991
.7	1. 4742			.2	1. 4906	.5	1. 4993
.8	1. 4744	77.0	1. 4825	.3	1. 4909	.6	1. 4996
.9	1. 4747	.1	1. 4827	.4	1. 4912	.7	1. 4999
		.2	1. 4830	.5	1. 4914	.8	1. 5001
74.0	1. 4749	.3	1. 4832	.6	1. 4917	.9	1. 5004
.1	1. 4752	.4	1. 4835	.7	1. 4919		
.2	1. 4754	.5	1. 4838	.8	1. 4922	84.0	1. 5007
.3	1. 4757	.6	1 4840	.9	1. 4925	.1	1. 5009
.4	1. 4759	.7	1. 4843			.2	1. 5012
.5	1. 4762	.8	1. 4845	81.0	1. 4927	.3	1. 5015
.6	1. 4764	.9	1. 4848	.1	1. 4930	.4	1. 5017
.7	1. 4767			.2	1. 4933	.5	1. 5020
.8	1. 4769	78.0	1. 4850	.3	1. 4935	.6	1. 0522
.9	1. 4772	.1	1. 4853	.4	1. 4938	.7	1. 5025
		.2	1. 4855	.5	1. 4941	.8	1. 5028
75.0	1. 4774	.3	1. 4858	.6	1. 4943	.9	1. 5030
.1	1. 4777	.4	1. 4860	.7	1. 4946		
.2	1. 4779	.5	1. 4863	.8	1. 4949	85.0	1 5033

TABLE 123.—*Correction table for determining the percentage of sucrose by means of the refractometer when the readings are made at temperatures other than 20° C*[1]

Temperature	Percentage of sucrose—														
	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70
	Subtract from the percentage of sucrose														
° C.															
10	0.50	0.54	0.58	0.61	0.64	0.66	0.68	0.70	0.72	0.73	0.74	0.75	0.76	0.78	0.79
11	.46	.49	.53	.55	.58	.60	.62	.64	.65	.66	.67	.68	.69	.70	.71
12	.42	.45	.48	.50	.52	.54	.56	.57	.58	.59	.60	.61	.61	.63	.63
13	.37	.40	.42	.44	.46	.48	.49	.50	.51	.52	.53	.54	.54	.55	.55
14	.33	.35	.37	.39	.40	.41	.42	.43	.44	.45	.45	.46	.46	.47	.48
15	.27	.29	.31	.33	.34	.34	.35	.36	.37	.37	.38	.39	.39	.40	.40
16	.22	.24	.25	.26	.27	.28	.28	.29	.30	.30	.30	.31	.31	.32	.32
17	.17	.18	.19	.20	.21	.21	.21	.22	.22	.23	.23	.23	.23	.24	.24
18	.12	.13	.13	.14	.14	.14	.14	.15	.15	.15	.15	.16	.16	.16	.16
19	.06	.06	.06	.07	.07	.07	.07	.08	.08	.08	.08	.08	.08	.08	.08
	Add to the percentage of sucrose														
21	0.06	0.07	0.07	0.07	0.07	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
22	.13	.13	.14	.14	.15	.15	.15	.15	.15	.16	.16	.16	.16	.16	.16
23	.19	.20	.21	.22	.22	.23	.23	.23	.23	.24	.24	.24	.24	.24	.24
24	.26	.27	.28	.29	.30	.30	.31	.31	.31	.31	.31	.32	.32	.32	.32
25	.33	.35	.36	.37	.38	.38	.39	.40	.40	.40	.40	.40	.40	.40	.40
26	.40	.42	.43	.44	.45	.46	.47	.48	.48	.48	.48	.48	.48	.48	.48
27	.48	.50	.52	.53	.54	.55	.55	.56	.56	.56	.56	.56	.56	.56	.56
28	.56	.57	.60	.61	.62	.63	.63	.64	.64	.64	.64	.64	.64	.64	.64
29	.64	.66	.68	.69	.71	.72	.72	.73	.73	.73	.73	.73	.73	.73	.73
30	.72	.74	.77	.78	.79	.80	.80	.81	.81	.81	.81	.81	.81	.81	.81

[1] International Temperature Correction Table, 1936, adopted by the International Commission for Uniform Methods of Sugar Analysis (Int. Sugar J. **39**, 24s, 1937).

TABLE 124.—*Refractive index of sucrose solutions at 28° C.*[1]

Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}
%		%		%		%	
0. 0	1. 33219	5. 0	. 33941	10. 0	. 34691	15. 0	. 35470
. 1	. 33233	. 1	. 33956	. 1	. 34706	. 1	. 35486
. 2	. 33248	. 2	. 33971	. 2	. 34722	. 2	. 35502
. 3	. 33262	. 3	. 33985	. 3	. 34737	. 3	. 35518
. 4	. 33276	. 4	. 34000	. 4	. 34752	. 4	. 35534
. 5	. 33291	. 5	. 34015	. 5	. 34767	. 5	. 35550
. 6	. 33305	. 6	. 34030	. 6	. 34783	. 6	. 35566
. 7	. 33319	. 7	. 34045	. 7	. 34798	. 7	. 35582
. 8	. 33333	. 8	. 34059	. 8	. 34813	. 8	. 35598
. 9	. 33348	. 9	. 34074	. 9	. 34829	. 9	. 35614
1. 0	. 33362	6. 0	. 34089	11. 0	. 34844	16. 0	. 35630
. 1	. 33376	. 1	. 34104	. 1	. 34859	. 1	. 35646
. 2	. 33391	. 2	. 34119	. 2	. 34875	. 2	. 35662
. 3	. 33405	. 3	. 34134	. 3	. 34891	. 3	. 35678
. 4	. 33420	. 4	. 34149	. 4	. 34906	. 4	. 35694
. 5	. 33434	. 5	. 34163	. 5	. 34921	. 5	. 35711
. 6	. 33448	. 6	. 34178	. 6	. 34937	. 6	. 35727
. 7	. 33463	. 7	. 34193	. 7	. 34953	. 7	. 35743
. 8	. 33477	. 8	. 34208	. 8	. 34968	. 8	. 35759
. 9	. 33492	. 9	. 34223	. 9	. 34983	. 9	. 35775
2. 0	. 33506	7. 0	. 34238	12. 0	. 34999	17. 0	1. 35791
. 1	. 33520	. 1	. 34253	. 1	. 35015	. 1	. 35807
. 2	. 33535	. 2	. 34268	. 2	. 35030	. 2	. 35823
. 3	. 33549	. 3	. 34283	. 3	. 35046	. 3	. 35840
. 4	. 33563	. 4	. 34298	. 4	. 35061	. 4	. 35856
. 5	. 33577	. 5	. 34313	. 5	. 35077	. 5	. 35872
. 6	. 33592	. 6	. 34327	. 6	. 35093	. 6	. 35888
. 7	. 33606	. 7	. 34342	. 7	. 35108	. 7	. 35904
. 8	. 33620	. 8	. 34357	. 8	. 35124	. 8	. 35921
. 9	. 33635	. 9	. 34372	. 9	. 35139	. 9	. 35937
3. 0	. 33649	8. 0	. 34387	13. 0	. 35155	18. 0	1. 35953
. 1	. 33664	. 1	. 34402	. 1	. 35171	. 1	. 35969
. 2	. 33678	. 2	. 34417	. 2	. 35186	. 2	. 35986
. 3	. 33693	. 3	. 34432	. 3	. 35202	. 3	. 36002
. 4	. 33707	. 4	. 34447	. 4	. 35218	. 4	. 36019
. 5	. 33722	. 5	. 34463	. 5	. 35233	. 5	. 36035
. 6	. 33737	. 6	. 34478	. 6	. 35249	. 6	. 36051
. 7	. 33751	. 7	. 34493	. 7	. 35265	. 7	. 36068
. 8	. 33766	. 8	. 34508	. 8	. 35281	. 8	. 36084
. 9	. 33780	. 9	. 34523	. 9	. 35296	. 9	. 36101
4. 0	. 33795	9. 0	. 34538	14. 0	. 35312	19. 0	1. 36117
. 1	. 33810	. 1	. 34553	. 1	. 35328	. 1	. 36133
. 2	. 33824	. 2	. 34569	. 2	. 35344	. 2	. 36150
. 3	. 33839	. 3	. 34584	. 3	. 35359	. 3	. 36167
. 4	. 33853	. 4	. 34599	. 4	. 35375	. 4	. 36183
. 5	. 33868	. 5	. 34615	. 5	. 35391	. 5	. 36199
. 6	. 33883	. 6	. 34630	. 6	. 35407	. 6	. 36216
. 7	. 33897	. 7	. 34645	. 7	. 35423	. 7	. 36233
. 8	. 33912	. 8	. 34660	. 8	. 35438	. 8	. 36249
. 9	. 33926	. 9	. 34676	. 9	. 35454	. 9	. 36265

[1] Int. Sugar J. **39**, 23s (1937).

TABLE 124.—*Refractive index of sucrose solutions at 28° C.*—Continued

Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}
%		%		%		%	
20. 0	1. 36282	25. 0	1. 3712	30. 0	1. 3800	35. 0	1. 3890
. 1	. 36299	. 1	. 3714	. 1	. 3802	. 1	. 3892
. 2	. 36315	. 2	. 3715	. 2	. 3804	. 2	. 3894
. 3	. 36332	. 3	. 3717	. 3	. 3805	. 3	. 3895
. 4	. 36348	. 4	. 3719	. 4	. 3807	. 4	. 3897
. 5	. 36365	. 5	. 3721	. 5	. 3809	. 5	. 3899
. 6	. 36382	. 6	. 3722	. 6	. 3811	. 6	. 3901
. 7	. 36398	. 7	. 3724	. 7	. 3813	. 7	. 3903
. 8	. 36415	. 8	. 3726	. 8	. 3814	. 8	. 3904
. 9	. 36431	. 9	. 3727	. 9	. 3816	. 9	. 3906
21. 0	1. 36448	26. 0	1. 3729	31. 0	1. 3818	36. 0	1. 3908
. 1	. 36465	. 1	. 3731	. 1	. 3820	. 1	. 3910
. 2	. 36481	. 2	. 3733	. 2	. 3821	. 2	. 3912
. 3	. 36498	. 3	. 3734	. 3	. 3823	3	. 3914
. 4	. 36515	. 4	. 3736	. 4	. 3825	. 4	. 3916
. 5	. 36531	. 5	. 3738	. 5	. 3827	. 5	. 3917
. 6	. 36548	. 6	. 3740	. 6	. 3828	. 6	. 3919
. 7	. 36565	. 7	. 3742	. 7	. 3830	. 7	. 3921
. 8	. 36582	. 8	. 3743	. 8	. 3832	. 8	. 3923
. 9	. 36598	. 9	. 3745	. 9	. 3833	. 9	. 3925
22. 0	1. 36615	27. 0	1. 3747	32. 0	1. 3835	37. 0	1. 3927
. 1	. 36632	. 1	. 3749	. 1	. 3837	. 1	. 3929
. 2	. 36648	. 2	. 3750	. 2	. 3839	. 2	. 3931
. 3	. 36665	. 3	. 3752	. 3	. 3840	. 3	. 3933
. 4	. 36682	. 4	. 3754	. 4	. 3842	. 4	. 3935
. 5	. 36699	. 5	. 3756	. 5	. 3844	. 5	. 3937
. 6	. 36715	. 6	. 3757	. 6	. 3846	. 6	. 3938
. 7	. 36732	. 7	. 3759	. 7	. 3848	. 7	. 3940
. 8	. 36749	. 8	. 3761	. 8	. 3849	. 8	. 3942
. 9	. 36765	. 9	. 3762	. 9	. 3851	. 9	. 3944
23. 0	1. 36782	28. 0	1. 3764	33. 0	1. 3853	38. 0	1. 3946
. 1	. 36799	. 1	. 3766	. 1	. 3855	. 1	. 3948
. 2	. 36816	. 2	. 3768	. 2	. 3857	. 2	. 3950
. 3	. 36833	. 3	. 3769	. 3	. 3858	. 3	. 3952
. 4	. 36850	. 4	. 3771	. 4	. 3860	. 4	. 3954
. 5	. 36867	. 5	. 3773	. 5	. 3862	. 5	. 3956
. 6	. 36884	. 6	. 3775	. 6	. 3864	. 6	. 3958
. 7	. 36901	. 7	. 3777	. 7	. 3866	. 7	. 3960
. 8	. 36918	. 8	. 3778	. 8	. 3867	. 8	. 3962
. 9	. 36935	. 9	. 3780	. 9	. 3869	. 9	. 3964
24. 0	1. 36952	29. 0	1. 3782	34. 0	1. 3871	39. 0	1. 3966
. 1	. 3697	. 1	. 3784	. 1	. 3873	. 1	. 3968
. 2	. 3699	. 2	. 3786	. 2	. 3875	2	. 3970
. 3	. 3700	. 3	. 3787	. 3	. 3877	. 3	. 3972
. 4	. 3702	. 4	. 3789	. 4	. 3879	. 4	. 3974
. 5	. 3704	. 5	. 3791	. 5	. 3881	. 5	. 3975
. 6	. 3705	. 6	. 3793	. 6	. 3882	. 6	. 3977
. 7	. 3707	. 7	. 3795	. 7	. 3884	. 7	. 3979
. 8	. 3709	. 8	. 3796	. 8	. 3886	. 8	. 3981
. 9	. 3710	. 9	. 3798	. 9	. 3888	. 9	. 3983

TABLE 124.—*Refractive index of sucrose solutions at 28° C.*—Continued

Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}
%		%		%		%	
40. 0	1. 3985	45. 0	1. 4083	50. 0	1. 4187	55. 0	1. 4293
. 1	. 3987	. 1	. 4085	. 1	. 4189	. 1	. 4295
. 2	. 3989	. 2	. 4087	. 2	. 4191	. 2	. 4297
. 3	. 3990	. 3	. 4089	. 3	. 4193	. 3	. 4300
. 4	. 3992	. 4	. 4091	. 4	. 4195	. 4	. 4302
. 5	. 3994	. 5	. 4093	. 5	. 4197	. 5	. 4304
. 6	. 3996	. 6	. 4096	. 6	. 4199	. 6	. 4306
. 7	. 3998	. 7	. 4098	. 7	. 4201	. 7	. 4308
. 8	. 3999	. 8	. 4100	. 8	. 4203	. 8	. 4311
. 9	. 4001	. 9	. 4102	. 9	. 4205	. 9	. 4313
41. 0	1. 4003	46. 0	1. 4104	51. 0	1. 4207	56. 0	1. 4315
. 1	. 4005	. 1	. 4106	. 1	. 4209	. 1	. 4317
. 2	. 4007	. 2	. 4108	. 2	. 4211	. 2	. 4319
. 3	. 4009	. 3	. 4110	. 3	. 4213	. 3	. 4322
. 4	. 4011	. 4	. 4112	. 4	. 4215	. 4	. 4324
. 5	. 4013	. 5	. 4114	. 5	. 4217	. 5	. 4326
. 6	. 4015	. 6	. 4116	. 6	. 4220	. 6	. 4328
. 7	. 4017	. 7	. 4118	. 7	. 4222	. 7	. 4330
. 8	. 4019	. 8	. 4120	. 8	. 4224	. 8	. 4333
. 9	. 4021	. 9	. 4122	. 9	. 4226	. 9	. 4335
42. 0	1. 4023	47. 0	1. 4124	52. 0	1. 4228	57. 0	1. 4337
. 1	. 4025	. 1	. 4126	. 1	. 4230	. 1	. 4339
. 2	. 4027	. 2	. 4128	. 2	. 4232	. 2	. 4341
. 3	. 4029	. 3	. 4130	. 3	. 4235	. 3	. 4344
. 4	. 4031	. 4	. 4132	. 4	. 4237	. 4	. 4346
. 5	. 4033	. 5	. 4135	. 5	. 4239	. 5	. 4348
. 6	. 4035	. 6	. 4137	. 6	. 4241	. 6	. 4350
. 7	. 4037	. 7	. 4139	. 7	. 4243	. 7	. 4352
. 8	. 4039	. 8	. 4141	. 8	. 4246	. 8	. 4355
. 9	. 4041	. 9	. 4143	. 9	. 4248	. 9	. 4357
43. 0	1. 4043	48. 0	1. 4145	53. 0	1. 4250	58. 0	1. 4359
. 1	. 4045	. 1	. 4147	. 1	. 4252	. 1	. 4361
. 2	. 4047	. 2	. 4149	. 2	. 4254	. 2	. 4364
. 3	. 4049	. 3	. 4151	. 3	. 4256	. 3	. 4366
. 4	. 4051	. 4	. 4153	. 4	. 4258	. 4	. 4368
. 5	. 4053	. 5	. 4155	. 5	. 4261	. 5	. 4371
. 6	. 4055	. 6	. 4158	. 6	. 4233	. 6	. 4373
. 7	. 4057	. 7	. 4160	. 7	. 4265	. 7	. 4375
. 8	. 4059	. 8	. 4162	. 8	. 4267	. 8	. 4377
. 9	. 4061	. 9	. 4164	. 9	. 4269	. 9	. 4380
44. 0	1. 4063	49. 0	1. 4166	54. 0	1. 4271	59. 0	1. 4382
. 1	. 4065	. 1	. 4168	. 1	. 4273	. 1	. 4384
. 2	. 4067	. 2	. 4170	. 2	. 4275	. 2	. 4386
. 3	. 4069	. 3	. 4172	. 3	. 4278	. 3	. 4388
. 4	. 4071	. 4	. 4174	. 4	. 4280	. 4	. 4390
. 5	. 4073	. 5	. 4177	. 5	. 4282	. 5	. 4393
. 6	. 4075	. 6	. 4179	. 6	. 4284	. 6	. 4395
. 7	. 4077	. 7	. 4181	. 7	. 4286	. 7	. 4397
. 8	. 4079	. 8	. 4183	. 8	. 4289	. 8	. 4399
. 9	. 4081	. 9	. 4185	. 9	. 4291	. 9	. 4401

TABLE 124.—*Refractive index of surcose solutions at 28° C.*—Continued

Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}
%		%		%		%	
60. 0	1. 4403	65. 0	1. 4517	70. 0	1. 4635	75. 0	1. 4758
. 1	. 4405	. 1	. 4519	. 1	. 4637	. 1	. 4761
. 2	. 4408	. 2	. 4522	. 2	. 4640	. 2	. 4763
. 3	. 4410	. 3	. 4524	. 3	. 4643	. 3	. 4765
. 4	. 4412	. 4	. 4526	. 4	. 4645	. 4	. 4768
. 5	. 4415	. 5	. 4529	. 5	. 4647	. 5	. 4771
. 6	. 4417	. 6	. 4531	. 6	. 4650	. 6	. 4773
. 7	. 4419	. 7	. 4533	. 7	. 4653	. 7	. 4775
. 8	. 4421	. 8	. 4535	. 8	. 4655	. 8	. 4778
. 9	. 4424	. 9	. 4538	. 9	. 4657	. 9	. 4781
61. 0	1. 4426	66. 0	1. 4540	71. 0	1. 4660	76. 0	1. 4783
. 1	. 4428	. 1	. 4542	. 1	. 4662	. 1	. 4786
. 2	. 4431	. 2	. 4545	. 2	. 4665	. 2	. 4788
. 3	. 4433	. 3	. 4547	. 3	. 4667	. 3	. 4791
. 4	. 4435	. 4	. 4550	. 4	. 4670	. 4	. 4793
. 5	. 4437	. 5	. 4552	. 5	. 4672	. 5	. 4796
. 6	. 4440	. 6	. 4554	. 6	. 4674	. 6	. 4799
. 7	. 4442	. 7	. 4557	. 7	. 4677	. 7	. 4801
. 8	. 4444	. 8	. 4559	. 8	. 4679	. 8	. 4804
. 9	. 4447	. 9	. 4562	. 9	. 4682	. 9	. 4806
62. 0	1. 4449	67. 0	1. 4564	72. 0	1. 4684	77. 0	1. 4809
. 1	. 4451	. 1	. 4566	. 1	. 4687	. 1	. 4811
. 2	. 4453	. 2	. 4569	. 2	. 4689	. 2	. 4814
. 3	. 4456	. 3	. 4571	. 3	. 4691	. 3	. 4817
. 4	. 4458	. 4	. 4574	. 4	. 4694	. 4	. 4819
. 5	. 4460	. 5	. 4576	. 5	. 4697	. 5	. 4821
. 6	. 4462	. 6	. 4578	. 6	. 4699	. 6	. 4824
. 7	. 4464	. 7	. 4581	. 7	. 4701	. 7	. 4827
. 8	. 4467	. 8	. 4583	. 8	. 4704	. 8	. 4829
. 9	. 4469	. 9	. 4586	. 9	. 4707	. 9	. 4831
63. 0	1. 4471	68. 0	1. 4588	73. 0	1. 4709	78. 0	1. 4834
. 1	. 4473	. 1	. 4590	. 1	. 4711	. 1	. 4837
. 2	. 4476	. 2	. 4593	. 2	. 4714	. 2	. 4839
. 3	. 4478	. 3	. 4595	. 3	. 4716	. 3	. 4842
. 4	. 4480	. 4	. 4598	. 4	. 4719	. 4	. 4844
. 5	. 4483	. 5	. 4600	. 5	. 4721	. 5	. 4847
. 6	. 4485	. 6	. 4602	. 6	. 4723	. 6	. 4850
. 7	. 4487	. 7	. 4605	. 7	. 4726	. 7	. 4852
. 8	. 4489	. 8	. 4607	. 8	. 4728	. 8	. 4855
. 9	. 4492	. 9	. 4610	. 9	. 4731	. 9	. 4857
64. 0	1. 4494	69. 0	1. 4612	74. 0	1. 4733	79. 0	1. 4860
. 1	. 4496	. 1	. 4614	. 1	. 4735	. 1	. 4862
. 2	. 4499	. 2	. 4617	. 2	. 4738	. 2	. 4865
. 5	. 4501	. 3	. 4619	. 3	. 4741	. 3	. 4860
. 4	. 4503	. 4	. 4621	. 4	. 4743	. 4	. 4877
. 5	. 4505	. 5	. 4623	. 5	. 4745	. 5	. 4872
. 6	. 4508	. 6	. 4626	. 6	. 4748	. 6	. 4874
. 7	. 4510	. 7	. 4628	. 7	. 4751	. 7	. 4877
. 8	. 4512	. 8	. 4630	. 8	. 4753	. 8	. 4879
. 9	. 4515	. 9	. 4633	. 9	. 4755	. 9	. 4882

TABLE 124.—*Refractive index of surcose solutions at 28° C.*—Continued

Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}	Sucrose by weight	Refractive index n_D^{28}
%		%		%		%	
80. 0	1. 4884	81. 3	1. 4918	82. 6	1. 4953	83. 9	1. 4987
. 1	. 4887	. 4	. 4921	. 7	. 4955		
. 2	. 4889	. 5	. 4923	. 8	. 4958	84. 0	1. 4990
. 3	. 4892	. 6	. 4926	. 9	. 4960	. 1	. 4993
. 4	. 4894	. 7	. 4929			. 2	. 4995
. 5	. 4897	. 8	. 4932	83. 0	1. 4963	. 3	. 4998
. 6	. 4900	. 9	. 4934	. 1	. 4966	. 4	. 5000
. 7	. 4902			. 2	. 4968	. 5	. 5003
. 8	. 4905	82. 0	1. 4937	. 3	. 4971	. 6	. 5006
. 9	. 4907	. 1	. 4940	. 4	. 4974	. 7	. 5008
		. 2	. 4942	. 5	. 4977	. 8	. 5011
81. 0	1. 4910	. 3	. 4945	. 6	. 4979	. 9	. 5013
. 1	. 4913	. 4	. 4947	. 7	. 4982		
. 2	. 4915	. 5	. 4950	. 8	. 4985	85. 0	1. 5016

TABLE 125.—*Correction table for determining the percentage of sucrose by means of the tropical model of refractometer when the readings are made at temperatures other than 28° C* [1]

Temperature	Percentage of sucrose														
	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70
	Subtract from percentage of sucrose														
°C															
20	0. 57	0. 59	0. 60	0. 61	0. 62	0. 63	0. 63	0. 64	0. 64	0. 64	0. 64	0. 64	0. 64	0. 65	0. 65
21	. 51	. 52	. 53	. 53	. 55	. 55	. 55	. 56	. 56	. 56	. 56	. 56	. 56	. 57	. 57
22	. 44	. 46	. 46	. 46	. 47	. 48	. 48	. 49	. 48	. 48	. 48	. 48	. 48	. 49	. 49
23	. 37	. 38	. 39	. 39	. 40	. 40	. 40	. 41	. 41	. 41	. 40	. 40	. 40	. 41	. 41
24	. 30	. 31	. 32	. 32	. 32	. 32	. 32	. 33	. 33	. 33	. 32	. 32	. 32	. 33	. 33
25	. 23	. 23	. 24	. 24	. 24	. 24	. 24	. 25	. 25	. 25	. 24	. 24	. 24	. 24	. 24
26	. 16	. 16	. 16	. 16	. 16	. 16	. 16	. 17	. 16	. 16	. 16	. 16	. 16	. 16	. 16
27	. 08	. 08	. 08	. 08	. 08	. 08	. 08	. 08	. 08	. 08	. 08	. 08	. 08	. 08	. 08
	Add to percentage of sucrose														
29	0. 09	0. 09	0. 09	0. 09	0. 09	0. 09	0. 09	0. 08	0. 08	0. 08	0. 08	0. 08	0. 08	0. 08	0. 08
30	. 17	. 17	. 17	. 17	. 17	. 17	. 17	. 17	. 17	. 17	. 17	. 17	. 17	. 17	. 17
31	. 26	. 26	. 26	. 26	. 26	. 26	. 26	25	. 25	. 25	. 25	. 25	. 25	. 25	. 25
32	. 35	. 35	. 35	. 35	. 35	. 34	. 34	. 34	. 34	. 34	. 34	. 33	. 33	. 33	. 33
33	. 44	. 44	. 44	. 44	. 44	. 43	. 43	. 43	. 43	. 42	. 42	. 42	. 42	. 42	. 42
34	. 54	. 54	. 53	. 53	. 53	. 52	. 52	. 52	. 52	. 51	. 51	. 50	. 50	. 50	. 50
35	. 63	. 63	. 63	. 62	. 62	. 62	. 61	. 61	. 61	60	. 60	. 59	. 59	. 59	. 58
36	. 73	. 73	. 73	. 72	. 72	. 72	. 71	. 70	. 70	. 69	. 69	. 68	. 67	. 67	. 67

[1] Int. Sugar J. **39,** 24s (1937).

TABLE 126.—*Determination of percentage of sucrose in sugar solutions from the readings of the Zeiss immersion refractometer at 20° C* [1]

Scale reading [2] at 20° C	n_D^{20}	Sucrose by weight	Scale reading at 20° C	n_D^{20}	Sucrose by weight	Scale reading at 20° C	n_D^{20}	Sucrose by weight
		%			%			%
14. 47	1. 33299	0	45	1. 34463	7. 91	76	1. 35606	15. 24
15	1. 33320	. 15	46	1. 34500	8. 15	77	1. 35642	15. 47
16	1. 33358	. 41	47	1. 34537	8. 39	78	1. 35678	15. 69
17	1. 33397	. 68	48	1. 34575	8. 64	79	1. 35714	15. 91
18	1. 33435	. 94	49	1. 34612	8. 89	80	1. 35750	16. 14
19	1. 33474	1. 21	50	1. 34650	9. 13	81	1. 35786	16. 36
20	1. 33513	1. 48	51	1. 34687	9. 38	82	1. 35822	16. 58
21	1. 33551	1. 74	52	1. 34724	9. 62	83	1. 35858	16. 81
22	1. 33590	2. 01	53	1. 34761	9. 86	84	1. 35894	17. 03
23	1. 33628	2. 27	54	1. 34798	10. 10	85	1. 35930	17. 25
24	1. 33667	2. 54	55	1. 34836	10. 34	86	1. 35966	17. 47
25	1. 33705	2. 80	56	1. 34873	10. 58	87	1. 36002	17. 69
26	1. 33743	3. 07	57	1. 34910	10. 82	88	1. 36038	17. 91
27	1. 33781	3. 33	58	1. 34947	11. 06	89	1. 36074	18. 12
28	1. 33820	3. 59	59	1. 34984	11. 30	90	1. 36109	18. 34
29	1. 33858	3. 85	60	1. 35021	11. 54	91	1. 36145	18. 56
30	1. 33896	4. 11	61	1. 35058	11. 78	92	1. 36181	18. 78
31	1. 33934	4. 36	62	1. 35095	12. 01	93	1. 36217	19. 00
32	1. 33972	4. 62	63	1. 35132	12. 25	94	1. 36252	19. 21
33	1. 34010	4. 88	64	1. 35169	12. 48	95	1. 36287	19. 42
34	1. 34048	5. 14	65	1. 35205	12. 72	96	1. 36323	19. 63
35	1. 34086	5. 40	66	1. 35242	12. 95	97	1. 36359	19. 85
36	1. 34124	5. 65	67	1. 35279	13. 18	98	1. 36394	20. 06
37	1. 34162	5. 91	68	1. 35316	13. 41	99	1. 36429	20. 27
38	1. 34199	6. 16	69	1. 35352	13. 64	100	1. 36464	20. 48
39	1. 34237	6. 41	70	1. 35388	13. 87	101	1. 36500	20. 69
40	1. 34275	6. 66	71	1. 35425	14. 10	102	1. 36535	20. 90
41	1. 34313	6. 91	72	1. 35461	14. 33	103	1. 36570	21. 11
42	1. 34350	7. 16	73	1. 35497	14. 56	104	1, 36605	21. 32
43	1. 34388	7. 41	74	1. 35533	14. 79	105	1. 36640	21. 53
44	1. 34426	7. 66	75	1. 35569	15. 01	-------	----------	------

[1] The values in this table were calculated by J. A. Mathews from the five-place indices of Schönrock as given by Landt, Z. Ver. deut. Zucker-Ind. **83**, 692 (1933).

[2] The scale readings refer only to the scale of arbitrary units proposed by Pulfrich, Z. angew. Chem. p. 1168 (1899). According to this scale, 14.5=1.33300, 50.0=1.34650, and 100.0=1.36464. If the immersion refractometer used is calibrated according to another arbitrary scale, the readings must be converted into refractive indices before this table is used to determine the percentage of sugar.

TABLE 127.—*Schönrock temperature corrections for determining refractive index of sucrose solutions by means of a refractometer when readings are made at temperatures other than 20° C.*

Temperature	Percentage of sucrose							
	0	5	10	15	20	25	30	35
	Subtract from observed index							
° *C*								
10	0. 00072	0. 00080	0. 00089	0. 00097	0. 00105	0. 00114	0. 00122	0. 00131
11	066	073	081	089	095	103	111	119
12	060	067	073	080	086	093	100	106
13	053	059	065	071	076	082	088	093
14	047	052	057	062	066	071	076	081
15	039	044	048	052	055	059	063	068
16	032	036	039	042	045	048	051	055
17	025	027	029	032	034	037	039	041
18	017	019	020	022	023	025	026	028
19	009	009	010	011	011	013	013	014
	Add to observed index							
21	0. 00009	0. 00010	0. 00011	0. 00011	0. 00012	0. 00013	0. 00013	0. 00014
22	018	020	021	023	024	026	027	028
23	028	029	032	035	037	039	041	043
24	038	041	043	046	049	052	055	058
25	048	052	055	059	062	066	069	073
26	058	063	067	071	075	080	084	088
27	069	075	079	084	089	094	099	103
28	080	086	092	097	102	108	113	119
29	092	099	105	111	117	123	129	135
30	104	111	118	124	131	137	144	150
31	117	124	131	138	155	152	159	166
32	129	137	144	152	160	167	175	182
33	142	151	158	167	175	183	191	199
34	155	164	172	181	190	198	207	215
35	169	178	137	196	205	214	223	232
36	182	192	202	211	221	230	240	249

TABLE 127.—*Schönrock temperature corrections for determining refractive index of sucrose solutions by means of a refractometer when readings are made at temperatures other than 20° C*—Continued

Temperature	Percentage of sucrose						
	40	45	50	55	60	65	70
	Subtract from observed index						
° *C*							
10	0. 00139	0. 00147	0. 00156	0. 00164	0. 00172	0. 00180	0. 00189
11	126	133	141	148	155	163	170
12	113	119	126	132	138	145	151
13	099	105	111	116	121	127	133
14	086	090	095	100	104	109	114
15	072	075	079	083	087	091	095
16	058	061	064	067	070	073	076
17	043	046	048	051	053	055	057
18	029	031	032	034	035	037	038
19	015	015	016	017	017	019	019
	Add to observed index						
21	0. 00015	0. 00015	0. 00017	0. 00017	0. 00018	0. 00019	0. 00019
22	030	031	033	034	036	037	038
23	045	047	049	051	054	055	057
24	060	063	066	069	072	074	077
25	076	079	083	087	090	093	097
26	092	096	100	104	108	112	116
27	108	113	117	122	127	131	135
28	124	129	134	140	145	150	155
29	140	146	151	158	163	169	175
30	156	163	169	176	182	188	195
31	173	180	187	194	201	207	215
32	190	197	205	212	220	227	235
33	207	215	223	231	239	247	255
34	224	232	241	249	258	266	275
35	241	250	259	268	277	286	295
36	259	268	278	287	296	306	315

TABLE 128.—*Method of obtaining* $-\log \mathbf{T}$

Log **T** for values of **T** from **T**=1.00 to **T**=0.100 may be taken directly from the table of mantissas below. For this range the characteristic is zero. Log **T** for values of **T** between **T**=0.100 and **T**=0.0000 is obtained by taking from the table of mantissas the decimal part of the logarithm corresponding to the number without regard to the position of the decimal point in the number and adding thereto the appropriate characteristic.

It should be remembered that if **T** is expressed as the fractional part of unity

Mantissas for numbers from 0 to 1

T	0	1	2	3	4
0. 10	−0. 00000	−0. 99568	−0. 99140	−0. 98716	−0. 98297
. 11	−. 95861	−. 95468	−. 95078	−. 94692	−. 94310
. 12	−. 92082	−. 91721	−. 91364	−. 91009	−. 90658
. 13	−. 88606	−. 88273	−. 87943	−. 87615	−. 87290
. 14	−. 85387	−. 85078	−. 84771	−. 84466	−. 84164
. 15	−. 82391	−. 82102	−. 81816	−. 81531	−. 81248
. 16	−. 79588	−. 79317	−. 79048	−. 78781	−. 78516
. 17	−. 76955	−. 76700	−. 76447	−. 76195	−. 75945
. 18	−. 74473	−. 74232	−. 73993	−. 73755	−. 73518
. 19	−. 72125	−. 71897	−. 71670	−. 71444	−. 71220
. 20	−. 69897	−. 69680	−. 69465	−. 69250	−. 69037
. 21	−. 67778	−. 67572	−. 67566	−. 67162	−. 66959
. 22	−. 65758	−. 65561	−. 65365	−. 65170	−. 64975
. 23	−. 63827	−. 63639	−. 63451	−. 63264	−. 63078
. 24	−. 61979	−. 61798	−. 61618	−. 61439	−. 61261
. 25	−. 60206	−. 60033	−. 59860	−. 59688	−. 59517
. 26	−. 58503	−. 58336	−. 58170	−. 58004	−. 57840
. 27	−. 56864	−. 56703	−. 56543	−. 56384	−. 56225
. 28	−. 55284	−. 55129	−. 54975	−. 54821	−. 54668
. 29	−. 53760	−. 53611	−. 53462	−. 53313	−. 53165
. 30	−. 52288	−. 52143	−. 51999	−. 51856	−. 51713
. 31	−. 50864	−. 50724	−. 50585	−. 50446	−. 50307
. 32	−. 49485	−. 49349	−. 49214	−. 49080	−. 48945
. 33	−. 48149	−. 48017	−. 47886	−. 47756	−. 47625
. 34	−. 46852	−. 46725	−. 46597	−. 46471	−. 46344
. 35	−. 45593	−. 45469	−. 45346	−. 45223	−. 45100
. 36	−. 44370	−. 44249	−. 44129	−. 44009	−. 43890
. 37	−. 43180	−. 43063	−. 42946	−. 42829	−. 42713
. 38	−. 42022	−. 41908	−. 41794	−. 41680	−. 41567
. 39	−. 40894	−. 40782	−. 40671	−. 40561	− 40450
. 40	−. 39794	−. 39686	−. 39577	−. 39469	−. 39362
. 41	−. 38722	−. 38616	−. 38510	−. 38405	−. 38300
. 42	−. 37675	−. 37572	−. 37469	−. 37366	−. 37263
. 43	−. 36653	−. 36552	−. 36452	−. 36351	− 36251
. 44	−. 35655	−. 35556	−. 35458	−. 35360	−. 35262
. 45	−. 34679	−. 34582	−. 34486	−. 34390	−. 34294
. 46	−. 33724	−. 33630	−. 33536	−. 33442	−. 33348
. 47	−. 32790	−. 32698	−. 32606	−. 32514	−. 32422
. 48	−. 31876	−. 31785	−. 31695	−. 31605	−. 31515
. 49	−. 30980	−. 30892	−. 30803	−. 30715	−. 30627
. 50	−. 30103	−. 30016	−. 29930	−. 29843	−. 29757
. 51	−. 29243	−. 29158	−. 29073	−. 28988	−. 28904
. 52	−. 28400	−. 28316	−. 28233	−. 28150	−. 28067
. 53	−. 27572	−. 27491	−. 27409	−. 27327	−. 27246
. 54	−. 26761	−. 26680	−. 26600	−. 26520	−. 26440

TABLE 128.—*Method of obtaining* —log **T**—Continued

the characteristic is equal to minus the number of zeros between the decimal point and the first significant figure. Thus, the characteristic of **T**=0.5 is 0; that of **T**=0.005 (0.5 percent) is −2; etc.

EXAMPLE 1.—To find −log **T** if **T**=0.00543. In the table of mantissas the mantissa corresponding to 543 (disregarding the position of the decimal point) is −0.26520. Since there are two zeros between the decimal point and the first significant figure the characteristic is −2. Adding these, log **T**=−2.26520 and −log **T**=+2.2652.

Mantissas for numbers from 0 to 1—Continued

T	5	6	7	8	9
0. 10	−0. 97881	−0. 97469	−0. 97062	−0. 96658	−0. 96257
. 11	−. 93930	−. 93554	−. 93181	−. 92812	−. 92445
. 12	−. 90309	−. 89963	−. 89620	−. 89279	−. 88941
. 13	−. 86967	−. 86646	−. 86328	−. 86012	−. 85699
. 14	−. 83863	−. 83565	−. 83268	−. 82974	−. 82681
. 15	−. 80967	−. 80688	−. 80410	−. 80134	−. 79860
. 16	−. 78252	−. 77989	−. 77728	−. 77469	−. 77211
. 17	−. 75696	−. 75449	−. 75203	−. 74958	−. 74715
. 18	−. 73283	−. 73049	−. 72816	−. 72584	−. 72354
. 19	−. 70992	−. 70774	−. 70553	−. 70333	−. 70115
. 20	−. 68825	−. 68613	−. 68403	−. 68194	−. 67985
. 21	−. 66756	−. 66555	−. 66354	−. 66154	−. 65956
. 22	−. 64782	−. 64589	−. 64397	−. 64207	−. 64016
. 23	−. 62893	−. 62709	−. 62525	−. 62342	−. 62160
. 24	−. 61083	−. 60906	−. 60730	−. 60555	−. 60380
. 25	−. 59346	−. 59176	−. 59007	−. 58838	−. 58670
. 26	−. 57675	−. 57512	−. 57349	−. 57187	−. 57025
. 27	−. 56067	−. 55909	−. 55752	−. 55596	−. 55440
. 28	−. 54516	−. 54363	−. 54212	−. 54061	−. 53910
. 29	−. 53018	−. 52871	−. 52724	−. 52578	−. 52433
. 30	−. 51570	−. 51428	−. 51286	−. 51145	−. 51004
. 31	−. 50169	−. 50031	−. 49894	−. 49757	−. 49621
. 32	−. 48812	−. 48678	−. 48545	−. 48413	−. 48280
. 33	−. 47496	−. 47366	−. 47237	−. 47108	−. 46980
. 34	−. 46218	−. 46092	−. 45967	−. 45842	−. 45717
. 35	−. 44977	−. 44855	−. 44733	−. 44612	−. 44491
. 36	−. 43771	−. 43652	−. 43533	−. 43415	−. 43297
. 37	−. 42597	−. 42481	−. 42366	−. 42251	−. 42136
. 38	−. 41454	−. 41341	−. 41229	−. 41117	−. 41005
. 39	−. 40340	−. 40230	−. 40121	−. 40012	−. 39903
. 40	−. 39254	−. 39147	−. 39041	−. 38934	−. 38828
. 41	−. 38195	−. 38091	−. 37986	−. 37882	−. 37779
. 42	−. 37161	−. 37059	−. 36957	−. 36856	−. 36754
. 43	−. 36151	−. 36051	−. 35952	−. 35853	−. 35754
. 44	−. 35164	−. 35067	−. 34969	−. 34872	−. 34775
. 45	−. 34199	−. 34104	−. 34008	−. 33913	−. 33819
. 46	−. 33255	−. 33161	−. 33068	−. 32975	−. 32883
. 47	−. 32331	−. 32239	−. 32148	−. 32057	−. 31966
. 48	−. 31426	−. 31336	−. 31247	−. 31158	−. 31069
. 49	−. 30539	−. 30452	−. 30364	−. 30277	−. 30190
. 50	−. 29671	−. 29585	−. 29499	−. 29416	−. 29328
. 51	−. 28819	−. 28735	−. 28651	−. 28567	−. 28483
. 52	−. 27984	−. 27901	−. 27819	−. 27737	−. 27654
. 53	−. 27165	−. 27084	−. 27003	−. 26922	−. 26841
. 54	−. 26360	−. 26281	−. 26201	−. 26122	−. 26043

TABLE 128.—*Mantissas for numbers from 0 to 1*—Continued

T	0	1	2	3	4
.55	—.25964	—.25885	—.25806	—.25727	—.25649
.56	—.25181	—.25104	—.25026	—.24949	—.24872
.57	—.24413	—.24336	—.24260	—.24185	—.24109
.58	—.23657	—.23582	—.23508	—.23433	—.23359
.59	—.22915	—.22841	—.22768	—.22695	—.22621
.60	—.22185	—.22113	—.22040	—.21968	—.21896
.61	—.21467	—.21396	—.21325	—.21254	—.21183
.62	—.20761	—.20691	—.20621	—.20551	—.20482
.63	—.20066	—.19997	—.19928	—.19860	—.19791
.64	—.19382	—.19314	—.19246	—.19179	—.19111
.65	—.18709	—.18642	—.18575	—.18509	—.18442
.66	—.18046	—.17980	—.17914	—.17849	—.17783
.67	—.17393	—.17328	—.17263	—.17198	—.17134
.68	—.16749	—.16685	—.16622	—.16558	—.16494
.69	—.16115	—.16052	—.15989	—.15927	—.15864
.70	—.15490	—.15428	—.15366	—.15304	—.15243
.71	—.14874	—.14813	—.14752	—.14691	—.14630
.72	—.14267	—.14206	—.14146	—.14086	—.14026
.73	—.13668	—.13608	—.13549	—.13490	—.13430
.74	—.13077	—.13018	—.12960	—.12901	—.12843
.75	—.12494	—.12436	—.12378	—.12321	—.12263
.76	—.11919	—.11862	—.11805	—.11748	—.11691
.77	—.11351	—.11295	—.11238	—.11182	—.11126
.78	—.10791	—.10735	—.10679	—.10624	—.10568
.79	—.10237	—.10182	—.10127	—.10073	—.10018
.80	—.09691	—.09637	—.09583	—.09528	—.09474
.81	—.09151	—.09098	—.09046	—.08991	—.08939
.82	—.08619	—.08566	—.08513	—.08460	—.08407
.83	—.08092	—.08040	—.07988	—.07935	—.07883
.84	—.07572	—.07520	—.07469	—.07417	—.07366
.85	—.07058	—.07007	—.06956	—.06905	—.06854
.86	—.06550	—.06500	—.06449	—.06399	—.06349
.87	—.06048	—.05998	—.05948	—.05899	—.05849
.88	—.05552	—.05502	—.05453	—.05404	—.05355
.89	—.05061	—.05012	—.04964	—.04915	—.04866
.90	—.04576	—.04528	—.04479	—.04431	—.04383
.91	—.04096	—.04048	—.04001	—.03953	—.03905
.92	—.03621	—.03574	—.03527	—.03480	—.03433
.93	—.03152	—.03105	—.03058	—.03012	—.02965
.94	—.02687	—.02641	—.02595	—.02549	—.02503
.95	—.02228	—.02182	—.02136	—.02091	—.02045
.96	—.01773	—.01728	—.01682	—.01637	—.01592
.97	—.01323	—.01278	—.01233	—.01189	—.01144
.98	—.00877	—.00833	—.00789	—.00745	—.00700
.99	—.00436	—.00393	—.00349	—.00305	—.00261

TABLE 128.—*Mantissas for numbers from 0 to 1*—Continued

T	5	6	7	8	9
.55	—.25571	—.25493	—.25414	—.25337	—.25259
.56	—.24795	—.24718	—.24642	—.24565	—.24489
.57	—.24033	—.23958	—.23882	—.23807	—.23732
.58	—.23284	—.23210	—.23136	—.23062	—.22988
.59	—.22548	—.22475	—.22403	—.22330	—.22257
.60	—.21824	—.21753	—.21681	—.21610	—.21538
.61	—.21112	—.21042	—.20971	—.20901	—.20831
.62	—.20412	—.20343	—.20273	—.20204	—.20135
.63	—.19723	—.19654	—.19586	—.19518	—.19450
.64	—.19044	—.18977	—.18910	—.18842	—.18776
.65	—.18376	—.18310	—.18243	—.18177	—.18111
.66	—.17718	—.17653	—.17587	—.17522	—.17457
.67	—.17070	—.17005	—.16941	—.16877	—.16813
.68	—.16431	—.16368	—.16304	—.16241	—.16178
.69	—.15802	—.15739	—.15677	—.15614	—.15552
.70	—.15181	—.15120	—.15058	—.14997	—.14935
.71	—.14569	—.14509	—.14448	—.14388	—.14327
.72	—.13966	—.13906	—.13847	—.13787	—.13727
.73	—.13371	—.13312	—.13253	—.13194	—.13136
.74	—.12784	—.12726	—.12668	—.12610	—.12552
.75	—.12205	—.12148	—.12090	—.12033	—.11976
.76	—.11634	—.11577	—.11520	—.11464	—.11407
.77	—.11070	—.11014	—.10958	—.10902	—.10846
.78	—.10513	—.10458	—.10403	—.10347	—.10292
.79	—.09963	—.09909	—.09864	—.09799	—.09745
.80	—.09420	—.09366	—.09313	—.09259	—.09205
.81	—.08884	—.08831	—.08778	—.08725	—.08672
.82	—.08355	—.08302	—.08249	—.08197	—.08145
.83	—.07831	—.07779	—.07727	—.07676	—.07624
.84	—.07314	—.07263	—.07212	—.07160	—.07109
.85	—.06803	—.06753	—.06702	—.06651	—.06601
.86	—.06298	—.06248	—.06198	—.06148	—.06098
.87	—.05799	—.05750	—.05700	—.05651	—.05601
.88	—.05306	—.05257	—.05208	—.05159	—.05110
.89	—.04818	—.04769	—.04721	—.04672	—.04624
.90	—.04335	—.04287	—.04239	—.04191	—.04144
.91	—.03858	—.03810	—.03763	—.03716	—.03668
.92	—.03386	—.03339	—.03292	—.03245	—.03198
.93	—.02919	—.02872	—.02826	—.02780	—.02733
.94	—.02457	—.02411	—.02365	—.02319	—.02273
.95	—.02000	—.01954	—.01909	—.01863	—.01818
.96	—.01547	—.01502	—.01457	—.01412	—.01368
.97	—.01100	—.01055	—.01011	—.00966	—.00922
.98	—.00656	—.00612	—.00568	—.00524	—.00480
.99	—.00218	—.00174	—.00130	—.00087	—.00043

323414°—42——44

TABLE 129.—*Refractive index of levulose solutions*

[All data computed from weights in air with brass weights. Immersion readings are referable solely to the scale of arbitrary units proposed by Pulfrich (Z. angew. Chem., p. 1186, 1899). According to this scale, 14.5=1.33300; 50.0=1.34650, and 100.0=1.36464]

Levulose by weight	n^{20}_D	Zeiss immersion reading, 20° C.	n^{25}_D	Zeiss immersion reading, 25° C.	$\frac{-\Delta n}{\Delta t^0}$	Levulose by weight	n^{20}_D	n^{25}_D	$\frac{-\Delta n}{\Delta t^0}$	Levulose by weight	n^{20}_D	n^{25}_D	$\frac{-\Delta n}{\Delta t^0}$
%					$\times 10^{-6}$	%			$\times 10^{-6}$	%			$\times 10^{-5}$
0	1.33300	14.50	1.33252	13.25	96	32	1.38385	1.38297	175	64	1.4479	1.4467	24
1	1.33442	18.18	1.33393	16.90	98	33	1.38564	1.38476	177	65	1.4501	1.4489	24
2	1.33585	21.87	1.33535	20.58	100	34	1.38745	1.38655	180	66	1.4524	1.4512	24
3	1.33729	25.63	1.33678	24.29	102	35	1.38927	1.38836	183	67	1.4547	1.4535	24
4	1.33874	29.42	1.33822	28.05	104	36	1.39111	1.39018	185	68	1.4569	1.4557	24
5	1.34020	33.26	1.33967	31.87	106	37	1.39295	1.39201	188	69	1.4592	1.4580	24
6	1.34167	37.14	1.34113	35.71	108	38	1.39481	1.39386	190	70	1.4615	1.4602	24
7	1.34315	41.05	1.34260	39.61	110	39	1.39669	1.39573	192	71	1.4638	1.4625	24
8	1.34464	45.03	1.34408	43.53	112	40	1.39858	1.39760	195	72	1.4661	1.4648	24
9	1.34614	49.05	1.34557	47.53	115	41	1.40048	1.39949	197	73	1.4684	1.4672	25
10	1.34765	53.11	1.34707	51.54	117	42	1.40239	1.40140	199	74	1.4708	1.4695	25
11	1.34917	57.19	1.34857	55.57	119	43	1.40432	1.40331	202	75	1.4731	1.4719	25
12	1.35070	61.32	1.35009	59.68	121	44	1.40625	1.40524	204	76	1.4755	1.4742	25
13	1.35224	65.51	1.35162	63.81	123	45	1.40821	1.40718	206	77	1.4779	1.4766	25
14	1.35379	69.75	1.35316	68.00	125	46	1.41018	1.40914	208	78	1.4803	1.4790	25
15	1.35534	74.03	1.35470	72.25	127	47	1.41216	1.41111	210	79	1.4827	1.4814	25
16	1.35691	78.36	1.35626	76.56	129	48	1.41415	1.41309	213	80	1.4851	1.4838	25
17	1.35849	82.75	1.35783	80.92	132	49	1.41616	1.41509	214	81	1.4875	1.4862	25
18	1.36008	87.17	1.35942	85.28	135	50	1.41818	1.41710	216	82	1.4900	1.4887	25
19	1.36169	91.64	1.36102	89.71	137	51	1.42021	1.41912	218	83	1.4924	1.4912	25
20	1.36332	96.14	1.36262	94.17	139	52	1.42226	1.42117	219	84	1.4949	1.4936	25
21	1.36496	100.72	1.36425	98.71	142	53	1.42432	1.42322	221	85	1.4974	1.4961	25
22	1.36659	105.37	1.36588	103.31	146	54	1.42640	1.42528	223	86	1.4999	1.4986	25
23	1.36827	-------	1.36753	-------	148	55	1.42848	1.42736	224	87	1.5024	1.5011	25
24	1.36996	-------	1.36921	-------	151	56	1.43058	1.42945	226	88	1.5049	1.5036	25
25	1.37166	-------	1.37088	-------	154	57	1.43270	1.43156	228	89	1.5074	1.5062	25
26	1.37336	-------	1.37258	-------	157	58	1.43482	1.43368	229	90	1.5100	1.5087	25
27	1.37506	-------	1.37426	-------	161	59	1.43696	1.43581	231	91	1.5126	1.5113	25
28	1.37680	-------	1.37598	-------	164	60	1.43913	1.43797	232	92	1.5151	1.5139	25
29	1.37854	-------	1.37771	-------	166	61	1.44130	1.44014	233	93	1.5177	1.5165	25
30	1.38030	-------	1.37945	-------	169	62	1.44348	1.44232	235	94	1.5203	1.5191	25
31	1.38207	-------	1.38121	-------	172	63	1.44569	1.44451	236	95	1.5230	1.5217	25

TABLE 130.—*Viscosity, in centipoises, of sucrose solutions*

[Recommended for use in the calibration of viscometers. These values are based upon measurements made at the National Bureau of Standards on solutions containing 20, 30, 40, 50, 60, 65, 70, and 75 percent of sucrose by weight in vacuo, using the value 1.0050 centipoises for water at 20° C, and are estimated to be accurate to about 0.1 percent]

Sucrose by weight in vacuo	Temperature in ° C										
	15	16	17	18	19	20	21	22	23	24	25
%											
20	2.268	2.200	2.135	2.073	2.014	1.957	1.902	1.850	1.800	1.752	1.706
1	2.372	2.300	2.232	2.166	2.104	2.044	1.986	1.932	1.879	1.828	1.780
2	2.484	2.408	2.336	2.267	2.201	2.137	2.077	2.019	1.963	1.909	1.858
3	2.605	2.525	2.448	2.375	2.305	2.238	2.174	2.112	2.053	1.997	1.943
4	2.736	2.650	2.569	2.491	2.417	2.346	2.278	2.213	2.151	2.091	2.034
5	2.877	2.786	2.700	2.617	2.538	2.463	2.391	2.322	2.255	2.192	2.131
6	3.029	2.933	2.841	2.753	2.669	2.589	2.512	2.439	2.369	2.301	2.237
7	3.195	3.092	2.994	2.900	2.811	2.725	2.644	2.566	2.491	2.419	2.351
8	3.374	3.264	3.159	3.060	2.964	2.873	2.786	2.703	2.623	2.547	2.474
9	3.569	3.452	3.340	3.233	3.131	3.034	2.941	2.852	2.767	2.685	2.608
30	3.782	3.656	3.536	3.422	3.312	3.208	3.109	3.014	2.923	2.836	2.752
1	4.014	3.879	3.750	3.627	3.510	3.398	3.291	3.189	3.092	2.999	2.910
2	4.267	4.122	3.983	3.851	3.725	3.605	3.490	3.381	3.276	3.176	3.081
3	4.545	4.388	4.239	4.096	3.960	3.831	3.708	3.590	3.478	3.370	3.267
4	4.851	4.681	4.519	4.365	4.219	4.079	3.946	3.818	3.697	3.582	3.471
5	5.189	5.005	4.829	4.662	4.503	4.352	4.208	4.070	3.939	3.814	3.694
6	5.561	5.361	5.170	4.989	4.817	4.653	4.496	4.347	4.205	4.070	3.940
7	5.974	5.755	5.548	5.350	5.162	4.984	4.814	4.652	4.498	4.350	4.210
8	6.433	6.194	5.967	5.751	5.546	5.351	5.165	4.988	4.820	4.660	4.507
9	6.943	6.680	6.432	6.195	5.971	5.758	5.555	5.362	5.178	5.003	4.836
40	7.515	7.226	6.952	6.692	6.445	6.210	5.988	5.776	5.574	5.382	5.200
1	8.158	7.839	7.535	7.248	6.976	6.717	6.471	6.238	6.016	5.805	5.604
2	8.882	8.527	8.190	7.872	7.570	7.284	7.013	6.755	6.510	6.277	6.056
3	9.698	9.303	8.929	8.574	8.239	7.922	7.620	7.335	7.064	6.807	6.561
4	10.62	10.18	9.762	9.366	8.992	8.639	8.304	7.987	7.685	7.399	7.127
5	11.67	11.17	10.70	10.26	9.844	9.449	9.074	8.721	8.385	8.067	7.764
6	12.86	12.30	11.77	11.28	10.81	10.37	9.947	9.551	9.176	8.820	8.482
7	14.22	13.59	13.00	12.44	11.91	11.41	10.94	10.49	10.07	9.674	9.296
8	15.78	15.07	14.40	13.76	13.17	12.60	12.07	11.57	11.09	10.65	10.22
9	17.59	16.77	16.00	15.28	14.61	13.97	13.37	12.80	12.26	11.76	11.28
50	19.67	18.74	17.87	17.04	16.27	15.54	14.86	14.21	13.60	13.03	12.49
1	22.10	21.03	20.03	19.08	18.20	17.36	16.58	15.84	15.15	14.50	13.88
2	24.94	23.70	22.54	21.46	20.44	19.48	18.58	17.73	16.94	16.19	15.48
3	28.28	26.84	25.50	24.24	23.06	21.95	20.91	19.94	19.02	18.16	17.35
4	32.23	30.55	28.98	27.51	26.14	24.86	23.64	22.52	21.46	20.47	19.53
5	36.92	34.95	33.11	31.39	29.79	28.28	26.88	25.57	24.33	23.17	22.09
6	42.54	40.21	38.04	36.01	34.12	32.36	30.71	29.17	27.73	26.37	25.10
7	49.32	46.55	43.97	41.56	39.32	37.23	35.29	33.47	31.77	30.18	28.69
8	57.55	54.23	51.13	48.26	45.59	43.10	40.79	38.63	36.61	34.73	32.97
9	67.63	63.61	59.88	56.42	53.21	50.22	47.45	44.87	42.45	40.21	38.11
60	80.09	75.18	70.63	66.43	62.54	58.93	55.58	52.47	49.57	46.87	44.36
1	95.62	89.57	84.00	78.85	74.09	69.68	65.59	61.81	58.29	55.02	51.98
2	115.1	107.6	100.7	94.34	88.47	83.03	78.02	73.37	69.07	65.08	61.37
3	139.9	130.5	121.8	113.9	106.6	99.80	93.57	87.82	82.51	77.58	73.02
4	171.6	159.7	148.7	138.7	129.5	121.0	113.2	106.0	99.41	93.28	87.62
5	212.8	197.5	183.5	170.7	158.9	148.2	138.3	129.2	120.9	113.2	106.1
6	266.8	246.9	228.8	212.3	197.2	183.3	170.7	159.1	148.4	138.7	129.7
7	338.7	312.5	288.7	267.0	247.4	229.4	213.0	198.0	184.3	171.7	160.2
8	435.6	400.5	368.9	340.2	314.2	290.5	269.0	249.3	231.4	215.0	200.1
9	568.0	520.6	477.8	439.2	404.3	372.7	344.0	317.9	294.2	272.6	252.9
70	752.2	687.0	628.3	575.5	527.9	485.0	446.2	411.1	379.2	350.2	323.9
1	1013.	921.3	839.4	766.0	700.1	640.8	587.5	539.3	495.8	456.4	420.7
2	1389.	1258.	1141.	1037.	944.3	860.9	786.1	719.0	658.6	604.1	554.9
3	1943.	1752.	1582.	1431.	1297.	1178.	1071.	975.6	890.0	813.1	744.1
4	2778.	2492.	2239.	2016.	1818.	1643.	1488.	1349.	1225.	1115.	1016.
5	4067.	3628.	3243.	2904.	2606.	2344.	2112.	1906.	1723.	1560.	1415.

TABLE 131.—*Viscosity, in centipoises, of sucrose solutions at 20° C relative to water* (η/η_{H_2O})

Sucrose by weight	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
%										
0	1.000	1.026	1.053	1.082	1.113	1.145	1.179	1.215	1.253	1.293
10	1.336	1.381	1.430	1.481	1.535	1.593	1.655	1.721	1.791	1.866
20	1.947	2.034	2.127	2.227	2.334	2.451	2.576	2.712	2.859	3.019
30	3.192	3.381	3.587	3.812	4.059	4.330	4.630	4.959	5.324	5.729
40	6.18	6.68	7.25	7.88	8.59	9.40	10.31	11.35	12.54	13.90
50	15.47	17.28	19.38	21.87	24.73	28.14	32.20	37.05	42.89	49.97
60	58.64	69.33	82.62	99.30	120.4	147.4	182.4	228.3	289.1	371.0
70	482.6	637.6	856.6	1,172	1,635	2,332	--------	--------	--------	--------

TABLE 132.—*Viscosity, in centipoises, of sucrose solutions from 0° to 40° C in 5-degree intervals*

[These values are based on the same measurements mentioned in table 130]

Sucrose by weight in vacuo	Temperature in ° C								
	0	5	10	15	20	25	30	35	40
%									
20	3.806	3.157	2.658	2.268	1.957	1.706	1.501	1.332	1.190
1	4.002	3.314	2.785	2.372	2.044	1.780	1.564	1.386	1.237
2	4.213	3.482	2.922	2.484	2.137	1.858	1.631	1.443	1.287
3	4.443	3.665	3.069	2.605	2.238	1.943	1.702	1.505	1.340
4	4.691	3.862	3.228	2.736	2.346	2.034	1.779	1.571	1.397
5	4.962	4.077	3.401	2.877	2.463	2.131	1.862	1.642	1.458
6	5.256	4.309	3.588	3.029	2.589	2.237	1.952	1.718	1.524
7	5.577	4.562	3.791	3.195	2.725	2.351	2.048	1.800	1.595
8	5.927	4.838	4.012	3.374	2.873	2.474	2.152	1.889	1.671
9	6.311	5.140	4.253	3.569	3.034	2.608	2.264	1.984	1.753
30	6.735	5.470	4.516	3.782	3.208	2.752	2.386	2.088	1.842
1	7.194	5.831	4.803	4.014	3.398	2.910	2.518	2.199	1.937
2	7.703	6.227	5.118	4.267	3.605	3.081	2.661	2.319	2.040
3	8.268	6.666	5.464	4.545	3.831	3.267	2.816	2.451	2.152
4	8.899	7.153	5.847	4.851	4.079	3.471	2.985	2.593	2.272
5	9.605	7.696	6.272	5.189	4.352	3.694	3.170	2.748	2.403
6	10.38	8.289	6.738	5.561	4.653	3.940	3.375	2.919	2.547
7	11.26	8.963	7.261	5.974	4.984	4.210	3.596	3.103	2.703
8	12.25	9.716	7.844	6.433	5.351	4.507	3.840	3.306	2.874
9	13.36	10.56	8.494	6.943	5.758	4.836	4.110	3.529	3.059
40	14.65	11.52	9.229	7.515	6.210	5.200	4.405	3.772	3.262
1	16.11	12.61	10.06	8.158	6.717	5.604	4.733	4.041	3.484
2	17.79	13.85	11.00	8.882	7.284	6.056	5.098	4.339	3.731
3	19.71	15.27	12.06	9.698	7.922	6.561	5.504	4.670	4.003
4	21.91	16.88	13.27	10.62	8.639	7.127	5.958	5.038	4.306
5	24.45	18.73	14.65	11.67	9.449	7.764	6.466	5.449	4.642
6	27.40	20.86	16.22	12.86	10.37	8.482	7.037	5.909	5.017
7	30.81	23.31	18.03	14.22	11.41	9.296	7.681	6.425	5.437
8	34.80	26.17	20.12	15.78	12.60	10.22	8.409	7.008	5.908
9	39.49	29.50	22.55	17.59	13.97	11.28	9.236	7.666	6.439
50	45.05	33.41	25.39	19.67	15.54	12.49	10.18	8.416	7.040
1	51.64	38.02	28.68	22.10	17.36	13.88	11.26	9.267	7.722
2	59.51	43.48	32.57	24.94	19.48	15.48	12.50	10.24	8.498
3	68.99	49.99	37.17	28.28	21.95	17.35	13.94	11.36	9.387
4	80.48	57.82	42.68	32.23	24.86	19.53	15.60	12.66	10.41
5	94.51	67.29	49.25	36.92	28.28	22.09	17.55	14.16	11.58
6	111.8	78.82	57.20	42.54	32.36	25.10	19.82	15.91	12.95
7	133.2	93.00	66.86	49.32	37.23	28.69	22.51	17.96	14.54
8	160.1	110.3	78.70	57.55	43.10	32.97	25.70	20.37	16.41
9	193.9	132.4	93.35	67.63	50.22	38.11	29.50	23.23	18.59
60	237.4	160.2	111.7	80.09	58.93	44.36	34.07	26.65	21.19
1	293.7	195.6	134.7	95.62	69.68	51.98	39.61	30.75	24.28
2	367.2	241.2	164.1	115.1	83.03	61.37	46.36	35.71	28.00
3	464.9	300.7	201.8	139.9	99.80	73.02	54.66	41.76	32.49
4	595.7	379.2	250.8	171.6	121.0	87.62	64.95	49.19	37.96
5	773.1	484.1	315.3	212.8	148.2	106.1	77.85	58.39	44.68
6	[a] 1,020	[a] 626.3	[a] 401.3	266.8	183.3	129.7	94.12	69.90	52.99
7	[a] 1,365	[a] 821.9	[a] 517.3	338.7	229.4	160.2	114.9	84.42	63.39
8	[a] 1,859	[a] 1,096	[a] 676.8	435.6	290.5	200.1	141.7	103.0	76.51
9	[a] 2,579	[a] 1,486	[a] 898.8	568.0	372.7	252.9	176.8	126.9	93.23
70	[a] 3,654	[a] 2,052	[a] 1,214	752.2	485.0	323.9	223.2	158.1	114.8
1	[a] 5,290	[a] 2,891	[a] 1,670	[a] 1,013	640.8	420.7	285.4	199.4	143.0
2	[a] 7,847	[a] 4,165	[a] 2,345	[a] 1,389	860.9	554.9	370.2	254.8	180.2
3	[a] 11,960	[a] 6,146	[a] 3,364	[a] 1,943	1,178	744.1	487.7	330.2	230.1
4	[a] 18,770	[a] 9,310	[a] 4,941	[a] 2,778	1,643	1,016	653.1	434.6	298.1
75	[a] 31,410	[a] 14,530	[a] 7,454	[a] 4,067	2,344	1,415	891.0	581.5	392.2

[a] Values extrapolated below the temperature range of the measurements.

TABLE 133. *Viscosity, in centipoises, of sucrose solutions, from 45° to 80° C in 5-degree intervals*

[These values are based in part on the measurements of Bingham and Jackson][1]

Sucrose by weight in vacuo	Temperature in °C							
	45	50	55	60	65	70	75	80
Percent								
20	1. 07	0. 97	0. 88	0. 81	0. 74	0. 68	0. 63	0. 59
1	1. 11	1. 00	. 91	. 84	. 77	. 71	. 65	. 61
2	1. 15	1. 04	. 95	. 87	. 79	. 73	. 68	. 63
3	1. 20	1. 09	. 98	. 90	. 82	. 76	. 70	. 65
4	1. 25	1. 13	1. 02	. 93	. 85	. 79	. 73	. 67
5	1. 30	1. 17	1. 06	. 97	. 89	. 82	. 75	. 70
6	1. 36	1. 22	1. 11	1. 01	. 92	. 85	. 78	. 72
7	1. 42	1. 28	1. 16	1. 05	. 96	. 88	. 81	. 75
8	1. 49	1. 34	1. 21	1. 10	1. 00	. 92	. 85	. 78
9	1. 56	1. 40	1. 26	1. 14	1. 04	. 96	. 88	. 81
30	1. 64	1. 47	1. 32	1. 20	1. 09	1. 00	. 92	. 85
1	1. 72	1. 54	1. 38	1. 25	1. 14	1. 04	. 96	. 88
2	1. 81	1. 61	1. 45	1. 31	1. 19	1. 09	1. 00	. 92
3	1. 90	1. 70	1. 52	1. 37	1. 25	1. 14	1. 04	. 96
4	2. 01	1. 79	1. 60	1. 44	1. 31	1. 19	1. 09	1. 00
5	2. 12	1. 88	1. 68	1. 51	1. 37	1. 25	1. 14	1. 05
6	2. 24	1. 99	1. 77	1. 59	1. 44	1. 31	1. 19	1. 10
7	2. 37	2. 10	1. 87	1. 68	1. 51	1. 37	1. 25	1. 15
8	2. 52	2. 22	1. 98	1. 77	1. 59	1. 44	1. 31	1. 20
9	2. 68	2. 36	2. 09	1. 87	1. 68	1. 52	1. 38	1. 26
40	2. 85	2. 50	2. 22	1. 98	1. 77	1. 60	1. 45	1. 32
1	3. 03	2. 66	2. 35	2. 09	1. 87	1. 69	1. 53	1. 39
2	3. 24	2. 83	2. 50	2. 22	1. 98	1. 78	1. 61	1. 46
3	3. 46	3. 02	2. 66	2. 36	2. 10	1. 89	1. 70	1. 54
4	3. 72	3. 23	2. 84	2. 51	2. 23	2. 00	1. 80	1. 63
5	3. 99	3. 47	3. 03	2. 67	2. 37	2. 12	1. 91	1. 72
6	4. 30	3. 72	3. 25	2. 86	2. 53	2. 26	2. 02	1. 83
7	4. 65	4. 01	3. 49	3. 06	2. 71	2. 41	2. 15	1. 94
8	5. 03	4. 33	3. 76	3. 29	2. 90	2. 57	2. 30	2. 06
9	5. 47	4. 69	4. 06	3. 54	3. 11	2. 75	2. 45	2. 20
50	5. 96	5. 09	4. 39	3. 82	3. 35	2. 95	2. 62	2. 35
1	6. 51	5. 54	4. 76	4. 13	3. 61	3. 18	2. 82	2. 51
2	7. 13	6. 05	5. 18	4. 48	3. 90	3. 43	3. 03	2. 70
3	7. 85	6. 63	5. 66	4. 88	4. 24	3. 71	3. 27	2. 90
4	8. 66	7. 29	6. 20	5. 32	4. 61	4. 02	3. 53	3. 13
5	9. 60	8. 04	6. 81	5. 83	5. 03	4. 37	3. 83	3. 38
6	10. 7	8. 91	7. 52	6. 40	5. 51	4. 77	4. 17	3. 67
7	11. 9	9. 91	8. 32	7. 06	6. 05	5. 22	4. 55	3. 99
8	13. 4	11. 1	9. 25	7. 82	6. 67	5. 74	4. 98	4. 35
9	15. 1	12. 4	10. 3	8. 68	7. 38	6. 32	5. 47	4. 76

[1] E. C. Bingham and R. F. Jackson, Bul. BS 14, 59 (1918) S295.

TABLE 133.—*Viscosity, in centipoises, of sucrose solutions, from 45° to 80° C in 5-degree intervals*—Continued

Sucrose by weight in vacuo	Temperature in °C							
	45	50	55	60	65	70	75	80
Percent								
60	17. 1	14. 0	11. 6	9. 69	8. 19	7. 00	6. 02	5. 22
1	19. 5	15. 8	13. 0	10. 9	9. 14	7. 77	6. 66	5. 76
2	22. 3	18. 0	14. 8	12. 2	10. 2	8. 66	7. 40	6. 37
3	25. 7	20. 6	16. 8	13. 8	11. 5	9. 71	8. 25	7. 07
4	29. 8	23. 8	19. 2	15. 7	13. 0	10. 9	9. 24	7. 89
5	34. 8	27. 6	22. 1	18. 0	14. 8	12. 4	10. 4	8. 84
6	40. 9	32. 2	25. 6	20. 7	17. 0	14. 1	11. 8	9. 96
7	48. 5	37. 8	29. 9	24. 0	19. 5	16. 1	13. 4	11. 3
8	58. 0	44. 8	35. 2	28. 0	22. 7	18. 5	15. 3	12. 8
9	70. 0	53. 5	41. 7	33. 0	26. 4	21. 5	17. 7	14. 7
70	85. 2	64. 6	49. 8	39. 1	31. 1	25. 1	20. 5	16. 9
1	105	78. 6	60. 1	46. 7	36. 8	29. 5	23. 9	19. 6
2	131	96. 8	73. 2	56. 3	44. 0	35. 0	28. 1	22. 9
3	165	121	90. 0	68. 6	53. 1	41. 8	33. 4	27. 0
4	210	152	112	84. 4	64. 8	50. 5	40. 0	32. 1
5	272	194	141	105	79. 8	61. 6	48. 3	38. 4

TABLE 134.—*Herzfeld table of solubility of sucrose in water at different temperatures*

Temperature	Sucrose in 100 g of solution	Sucrose dissolved by 100 g of water	Water corresponding to 1 g of dissolved sucrose	d_4^{20}, solution [1]
° C	g	g	g	
0	64. 18	179. 2	0. 5580	1. 31131
5	64. 87	184. 7	. 5414	1. 31521
10	65. 58	190. 5	. 5249	1. 31980
15	66. 30	197. 0	. 5076	1. 32420
20	67. 09	203. 9	. 4904	1. 32905
25	67. 89	211. 4	. 4730	1. 33398
30	68. 70	219. 5	. 4556	1. 33894
35	69. 55	228. 4	. 4378	1. 34430
40	70. 42	238. 1	. 4200	1. 34975
45	71. 32	248. 7	. 4021	1. 35541
50	72. 25	260. 4	. 3840	1. 36130
55	73. 20	273. 1	. 3662	1. 36735
60	74. 18	287. 3	. 3418	1. 37363
65	75. 18	302. 9	. 3301	1. 38007
70	76. 22	320. 5	. 3120	1. 38681
75	77. 27	339. 9	. 2942	1. 39366
80	78. 36	362. 1	. 2762	1. 40081
85	79. 46	386. 8	. 2585	1. 40807
90	80. 61	415. 7	. 2406	1. 41571
95	81. 77	448. 6	. 2229	1. 42346
100	82. 97	487. 2	. 2053	1. 43154

[1] Percentages of sugar calculated from vacuum weights.

TABLE 135.—*Solubility of sucrose in pure water* [1]

[Grams of sugar per 100 g of water]

Temperature	Flourens, 1876	Herzfeld, 1892	Horsin-Déon	Scott-Macfie	Lebedev, 1908	Mondain-Monval, 1924	Grut, 1936	Hruby-Kasjanov, 1936
° C								
0	183	179. 2	183	163				
. 9						181		
10	190	190. 5	190	179				
15. 8						196		
20	199	203. 9	199	197			201	
25. 6						211		
30	213	219. 5	213	216	220		218	
30. 5						218		
40	231	238. 1	231	239			238	
50	255	260. 4	255	266	258		2 3	260
60	285	287. 3	283	296			293	
70	319	320. 5	319	333	330		330	
80	362	362. 1	362	376			390	373
90	415	415. 7	415	430				
100	471	487. 2	485	497				

[1] Compiled and bibliography supplied by R. Hruby and V. Kasjanov, Int. Sugar J. **42**, 21 (1940); Z. Zuckerind. Čechoslovak. Rep. **63**, 187 (1939).

TABLE 136.—*Velocity of crystallization according to Kukharenko, and concentration data for pure sucrose in water*

[Concentration data for solutions of pure sucrose in water for 10-degree intervals of temperature and for 0.005-intervals of Kukharenko's coefficient of supersaturation, $k=s'/s_t$, as based upon Herzfeld's table of solubilities of sucrose, together with the corresponding velocities of crystallization according to Kukharenko, where K has the dimensions $mg/(m^2 \times min)$. The "hypothetical yield at 20°, y_{20}," is the quantity given in column 13 but expressed as a percentage of the total quantity of sucrose present in 100 g of water, as given in column 11. The "oversaturation, e_{20}," in column 15 is the same quantity expressed as a percentage of 203.9 g, the weight of sucrose required to saturate 100 g of water at 20°, while "e_t" in column 16 is the percentage of sucrose dissolved in excess of saturation requirements at the temperature t; or, stated as an equation, $e_t=100(c'-c_t)/c_t$. Therefore, e_t is the quantity given in column 12 expressed not in grams but as a percentage of c_t when the unit weight of water is 100 g. The symbols used in the various equations have the following significance:

c' = weight of sucrose dissolved in unit weight of water in the given solution.
c_t = weight of sucrose required to saturate unit weight of water at the temerature t, as derived from Herzfeld's table of solubilities.
m^2 = total area of the erystal surface, expressed in square meters.
mg = weight of sucrose deposited on the erystals of m^2 surfaee area, expressed in mg.
min = time required to deposite the given weight of sucrose, expressed in minutes.
s' = pereentage of sucrose contained in the given solution.
s_t = percentage of suerose contained in a solution which is just saturated at the temperature t.]

Temperature	Supersaturation	Sugar	Water to 1 kg of sugar	Formula weights per kilogram of solution			Mole fraction		In 1 kg of water	In 100 g of water			Hypothetical yield at 20° C	Oversaturation		Crystallization velocity
				Sugar	Water	Total	Sugar	Water		Total	Excess at— t	Excess at— 20°		e_{20}	e_t	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
° C	k	*Per-cent*	*g*	*Moles*	*Moles*	*Moles*	*Per-cent*	*Per-cent*	*M*	*g*	*g*	*g*	*Per-cent*	*Per-cent*	*Per-cent*	*K*
20	1.000	67.09	490.5	1.96	18.27	20.23	9.7	91.3	5.96	203.9	0	0	0	0	0	0
	1.005	67.43	483.1	1.97	18.08	20.05	9.8	90.2	6.05	207.0	3.1	3.1	1.5	1.5	1.5	40
	1.010	67.76	475.8	1.98	17.89	19.87	10.0	90.0	6.14	210.2	6.3	6.3	3.0	3.1	3.1	80
	1.015	68.10	468.5	1.99	17.71	19.70	10.1	89.9	6.24	213.4	9.6	9.6	4.5	4.7	4.7	120
	1.020	68.43	461.3	2.00	17.52	19.52	10.2	89.8	6.33	216.8	12.9	12.9	6.0	6.3	6.3	150
	1.025	68.77	454.2	2.01	17.34	19.35	10.4	89.6	6.43	220.2	16.3	16.3	7.4	8.0	8.0	190
	1.030	69.10	447.1	2.02	17.15	19.17	10.5	89.5	6.53	223.7	19.8	19.8	8.9	9.7	9.7	230
	1.035	69.44	440.1	2.03	16.96	18.99	10.7	89.3	6.64	227.2	23.3	23.3	10.3	11.5	11.5	275
	1.040	69.77	433.2	2.04	16.78	18.82	10.8	89.2	6.74	230.8	27.0	27.0	11.7	13.2	13.2	320
	1.045	70.11	426.4	2.05	16.59	18.64	11.0	89.0	6.85	234.6	30.7	30.7	13.1	15.1	15.1	360
	1.050	70.45	419.5	2.06	16.41	18.47	11.2	88.8	6.96	238.4	34.5	34.5	14.5	16.9	16.9	420
	1.055	70.78	412.8	2.07	16.22	18.29	11.3	88.7	7.08	242.2	38.4	38.4	15.8	18.8	18.8	480
	1.060	71.12	406.2	2.08	16.03	18.11	11.5	88.5	7.19	246.2	42.3	42.3	17.2	20.8	20.8	525
	1.065	71.45	399.6	2.09	15.85	17.94	11.6	88.4	7.31	250.3	46.4	46.4	18.5	22.8	22.8	575
	1.070	71.79	393.0	2.10	15.66	17.76	11.8	88.2	7.43	254.4	50.6	50.6	19.9	24.8	24.8	620
30	1.000	68.70	455.6	2.01	17.37	19.38	10.3	89.7	6.41	219.5	0	15.6	7.1	7.7	0	0
	1.005	69.04	448.4	2.02	17.18	19.20	10.5	89.5	6.52	223.1	3.6	19.2	8.6	9.4	1.6	75
	1.010	69.39	441.2	2.03	16.99	19.02	10.7	89.3	6.62	226.7	7.2	22.8	10.1	11.2	3.3	150
	1.015	69.73	434.1	2.04	16.80	18.84	10.8	89.2	6.73	230.4	10.9	26.5	11.5	13.0	5.0	255
	1.020	70.07	427.1	2.05	16.61	18.66	11.0	89.0	6.84	234.2	14.7	30.3	12.9	14.9	6.7	380
	1.025	70.42	420.1	2.06	16.42	18.48	11.2	88.8	6.95	238.0	18.6	34.2	14.4	16.8	8.5	495
	1.030	70.76	413.2	2.07	16.23	18.30	11.3	88.7	7.07	242.0	22.5	38.2	15.8	18.7	10.3	625
	1.035	71.11	406.4	2.08	16.04	18.12	11.5	88.5	7.19	246.1	26.6	42.2	17.2	20.7	12.1	755
	1.040	71.45	399.6	2.09	15.85	17.94	11.6	88.4	7.31	250.2	30.8	46.4	18.5	22.8	14.0	910
	1.045	71.79	392.9	2.10	15.66	17.76	11.8	88.2	7.44	254.5	35.0	50.7	19.9	24.9	16.0	1,115
	1.050	72.14	386.3	2.11	15.47	17.58	12.0	88.0	7.56	258.9	39.4	55.0	21.3	27.0	17.9	1,320
	1.055	72.48	379.7	2.12	15.28	17.40	12.2	87.8	7.69	263.4	43.9	59.5	22.6	29.2	20.0	------
	1.060	72.82	373.2	2.13	15.09	17.22	12.4	87.6	7.83	267.9	48.5	64.1	23.9	31.4	22.1	------
	1.065	73.17	366.8	2.14	14.89	17.03	12.6	87.4	7.97	272.7	53.2	68.8	25.2	33.8	24.2	------
	1.070	73.51	360.4	2.15	14.70	16.85	12.8	87.2	8.11	277.5	58.0	73.6	26.5	36.1	26.4	------

TABLE 136.—*Velocity of crystallization according to Kukharenko, and concentration data for pure sucrose in water*—Continued

Temperature	Supersaturation	Sugar	Water to 1 kg of sugar	Formula weights per kilogram of solution			Mole fraction		In 1 kg of water	In 100 g of water			Hypothetical yield at 20° C	Oversaturation		Crystallization velocity
				Sugar	Water	Total	Sugar	Water		Total	Excess at— t	Excess at— 20°		ϵ_{20}	ϵ_t	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
°C	k	Per-cent	g	Moles	Moles	Moles	Per-cent	Per-cent	M	g	g	g	Per-cent	Per-cent	Per-cent	K
40	1.000	70.42	420.1	2.06	16.42	18.48	11.1	88.9	6.96	238.1	0	34.2	14.4	16.8	0	0
	1.005	70.77	413.0	2.07	16.22	18.29	11.3	88.7	7.07	242.1	4.1	38.3	15.8	18.8	1.7	145
	1.010	71.12	406.0	2.08	16.03	18.11	11.5	88.5	7.20	246.3	8.2	42.5	17.2	20.8	3.5	285
	1.015	71.48	399.1	2.09	15.83	17.92	11.7	88.3	7.32	250.6	12.5	46.7	18.6	22.9	5.3	490
	1.020	71.83	392.2	2.10	15.64	17.74	11.8	88.2	7.45	255.0	16.9	51.1	20.0	25.1	7.1	675
	1.025	72.18	385.4	2.11	15.44	17.55	12.0	88.0	7.58	259.5	21.4	55.6	21.1	27.3	9.0	855
	1.030	72.53	378.7	2.12	15.25	17.37	12.2	87.8	7.71	264.1	26.0	60.2	22.8	29.5	10.9	1,060
	1.035	72.89	372.0	2.13	15.05	17.18	12.4	87.6	7.85	268.8	30.7	64.9	24.2	31.9	12.9	1,300
	1.040	73.24	365.4	2.14	14.86	17.00	12.6	87.4	7.99	273.7	35.6	69.8	25.5	34.2	15.0	1,540
	1.045	73.59	358.9	2.15	14.66	16.81	12.8	87.2	8.14	278.6	40.6	74.8	26.8	36.7	17.0	1,800
	1.050	73.94	352.4	2.16	14.46	16.62	13.0	87.0	8.29	283.7	45.7	79.9	28.2	39.2	19.2	2,055
	1.055	74.29	346.0	2.17	14.27	16.44	13.2	86.8	8.44	289.0	50.9	85.1	29.5	41.8	21.4	2,580
	1.060	74.65	339.7	2.18	14.07	16.25	13.4	86.6	8.60	294.4	56.3	90.5	30.8	44.4	23.7	------
	1.065	75.00	333.4	2.19	13.88	16.07	13.6	86.4	8.76	300.0	61.9	96.1	32.0	47.1	26.0	------
	1.070	75.35	327.2	2.20	13.68	15.88	13.9	86.1	8.93	305.7	67.6	101.8	33.3	49.9	28.4	------
50	1.000	72.25	384.1	2.11	15.40	17.51	12.1	87.9	7.61	260.4	0	56.5	21.7	27.7	0	0
	1.005	72.61	377.2	2.12	15.20	17.32	12.2	87.8	7.75	265.1	4.8	61.3	23.1	30.1	1.8	240
	1.010	72.97	370.4	2.13	15.00	17.13	12.4	87.6	7.89	270.0	9.6	66.1	24.5	32.4	3.7	490
	1.015	73.33	363.6	2.14	14.80	16.94	12.6	87.4	8.03	275.0	14.7	71.2	25.9	34.9	5.6	800
	1.020	73.70	356.9	2.15	14.60	16.75	12.9	87.1	8.18	280.2	19.8	76.3	27.2	37.4	7.6	1,200
	1.025	74.06	350.3	2.16	14.40	16.56	13.1	86.9	8.34	285.5	25.1	81.6	28.6	40.0	9.6	1,800
	1.030	74.42	343.8	2.17	14.20	16.37	13.3	86.7	8.50	290.9	30.5	87.0	29.9	42.7	11.7	2,300
	1.035	74.78	337.3	2.19	14.00	16.19	13.5	86.5	8.66	296.5	36.1	92.6	31.2	45.4	13.9	2,870
	1.040	75.14	330.8	2.20	13.80	16.00	13.7	86.3	8.83	302.3	41.9	98.4	32.6	48.3	16.1	3,510
	1.045	75.50	324.5	2.21	13.60	15.81	14.0	86.0	9.00	308.2	47.8	104.3	33.9	51.2	18.4	4,060
	1.050	75.86	318.2	2.22	13.40	15.62	14.2	85.8	9.18	314.3	53.9	110.4	35.1	54.2	20.7	------
	1.055	76.22	312.0	2.23	13.20	15.43	14.4	85.6	9.37	320.6	60.2	116.7	36.4	57.3	23.1	------
	1.060	76.59	305.7	2.24	13.00	15.24	14.7	85.3	9.56	327.1	66.7	123.2	37.7	60.4	25.6	------
	1.065	76.95	299.6	2.25	12.80	15.05	14.9	85.1	9.75	333.8	73.4	129.9	38.9	63.7	28.2	------
	1.070	77.31	293.5	2.26	12.60	14.86	15.2	84.8	9.95	340.7	80.3	136.8	40.2	67.1	30.9	------
60	1.000	74.18	348.1	2.17	14.33	16.50	13.2	86.8	8.39	287.3	0	83.4	29.0	40.9	0	0
	1.005	74.55	341.4	2.18	14.13	16.31	13.4	86.6	8.56	292.9	5.6	89.1	30.4	43.7	2.0	340
	1.010	74.92	334.7	2.19	13.92	16.11	13.6	86.4	8.73	298.8	11.5	94.9	31.8	46.6	4.0	720
	1.015	75.29	328.1	2.20	13.71	15.91	13.8	86.2	8.90	304.7	17.4	100.9	33.1	49.5	6.1	1,340
	1.020	75.66	321.6	2.21	13.51	15.72	14.1	85.9	9.08	310.9	23.6	107.1	34.4	52.5	8.2	2,210
	1.025	76.04	315.2	2.22	13.30	15.52	14.3	85.7	9.27	317.3	30.0	113.4	35.8	55.6	10.4	3,100
	1.030	76.41	308.8	2.23	13.10	15.33	14.6	85.4	9.46	323.8	36.5	120.0	37.1	58.8	12.7	------
	1.035	76.78	302.5	2.24	12.89	15.13	14.8	85.2	9.66	330.6	43.3	126.7	38.3	62.2	15.1	------
	1.040	77.15	296.2	2.25	12.69	14.94	15.1	84.9	9.86	337.6	50.3	133.7	39.6	65.6	17.5	------
	1.045	77.52	290.0	2.27	12.48	14.75	15.4	84.6	10.07	344.8	57.5	140.9	40.9	69.1	20.0	------
	1.050	77.89	283.9	2.28	12.27	14.55	15.6	84.4	10.29	352.3	65.0	148.4	42.1	72.8	22.6	------
	1.055	78.26	277.8	2.29	12.07	14.36	15.9	84.1	10.52	360.0	72.7	156.1	43.4	76.6	25.3	------
	1.060	78.63	271.8	2.30	11.86	14.16	16.2	83.8	10.75	368.0	80.7	164.1	44.6	80.5	28.1	------
	1.065	79.00	265.8	2.31	11.66	13.97	16.5	83.5	10.99	376.2	88.9	172.4	45.8	84.6	31.0	------
	1.070	79.37	259.9	2.32	11.45	13.77	16.8	83.2	11.24	384.8	97.5	180.9	47.0	88.8	33.9	------
70	1.000	76.22	312.0	2.23	13.20	15.43	14.4	85.6	9.36	320.5	0	116.7	36.4	57.2	0	0
	1.005	76.60	305.5	2.24	12.99	15.23	14.7	85.3	9.56	327.4	6.9	123.5	37.7	60.6	2.1	850
	1.010	76.98	299.0	2.25	12.78	15.03	15.0	85.0	9.77	334.4	13.9	130.6	39.0	64.1	4.3	1,700
	1.015	77.36	292.6	2.26	12.57	14.83	15.2	84.8	9.98	341.8	21.2	137.9	40.4	67.6	6.6	2,564
	1.020	77.74	286.3	2.27	12.35	14.62	15.5	84.5	10.2	1349.3	28.8	145.5	41.6	71.4	9.0	4,000
	1.025	78.13	280.0	2.28	12.14	14.42	15.8	84.2	10.43	357.2	36.7	153.3	42.9	75.2	11.4	------
	1.030	78.51	273.8	2.29	11.93	14.22	16.1	83.9	10.67	365.3	44.8	161.4	44.2	79.2	14.0	------
	1.035	78.89	267.6	2.31	11.72	14.03	16.4	83.6	10.92	373.7	53.1	169.8	45.4	83.3	16.6	------
	1.040	79.27	261.5	2.32	11.51	13.83	16.8	83.2	11.17	382.4	61.9	178.5	46.7	87.6	19.3	------
	1.045	79.65	255.5	2.33	11.30	13.63	17.1	82.9	11.43	391.4	70.9	187.5	47.9	92.0	22.1	------
	1.050	80.03	249.5	2.34	11.08	13.42	17.4	82.6	11.71	400.8	80.3	196.9	49.1	96.6	25.0	------
	1.055	80.41	243.6	2.35	10.87	13.22	17.8	82.2	11.99	410.5	90.0	206.7	50.3	101.4	28.1	------
	1.060	80.79	237.7	2.36	10.66	13.02	18.1	81.9	12.29	420.6	100.1	216.8	51.5	106.3	31.2	------
	1.065	81.17	231.9	2.37	10.45	12.82	18.5	81.5	12.60	431.2	110.7	227.3	52.7	111.5	34.5	------
	1.070	81.56	226.2	2.38	10.24	12.62	18.9	81.1	12.92	442.2	121.7	238.3	53.9	116.9	38.0	------

TABLE 137.—*Solubility of dextrose in water*

Temperature	Solid phase	Dextrose in solution [1]	Dextrose per 100 g of water
°C		*Percent*	*g*
−0.772	Ice	6.83	
−2.117	do	16.65	
−2.305	do	17.59	
−5.605	do	33.02	
−5.3	Cryohydrate	31.75	
0.50	α-$C_6H_{12}O_6.H_2O$	35.2	54.32
22.98	do	49.37	97.51
28.07	do	52.99	112.72
30.00	do	54.64	120.46
35.00	do	58.02	138.21
40.40	do	62.13	164.06
41.45	do	62.82	168.96
45.00	do	65.71	191.63
50.00	Transition	70.91	243.76
28.00	α-$C_6H_{12}O_6$	67.0	203
40.00	do	67.6	209
45.00	Metastable	69.69	230
55.22	α-$C_6H_{12}O_6$	73.08	261.7
64.75	do	76.36	323.0
70.2	do	78.23	359.3
80.5	do	81.49	440.2
90.8	do	84.90	562.3

[1] Estimated as anhydrous sugar.

TABLE 138.—*Solubility of levulose in water*

Computed by means of the equation $C=0.150103t^2-0.814t+331.023$ derived by the method of least squares from three observed values, as follows: [1]

t	Percentage of levulose	C=g of levulose/100 g of water	Molecular weights used
°C			
20	78. 94	374. 78	Levulose 180. 1572
40	84. 34	538. 63	Water 18. 0162
55	88. 10	740. 32	

[1] BS Sci. Pap. **20**, 587 (1926) S519.

TABLE 138.—*Solubility of levulose in water*—Continued

Temperature	Basis of computation									
	Composition		Water to 1 kg. levulose	Number of molecular weights in 1 kg of solution			Mole fraction		Concentration of levulose in—	
	Levulose	Water		Levulose	Water	Total	Levulose	Water	1 kg of water	100 g of water
°C	*Percent*	*Percent*	*g*	*Moles*	*Moles*	*Moles*	*Percent*	*Percent*	*Moles*	*g*
20	78. 94	21. 06	266. 8	4. 38	11. 69	16. 07	27. 26	72. 74	20. 80	374. 78
21	79. 17	20. 83	263. 1	4. 39	11. 56	15. 95	27. 52	72. 48	21. 10	380. 12
22	79. 41	20. 59	259. 3	4. 41	11. 43	15. 84	27. 84	72. 16	21. 41	385. 77
23	79. 66	20. 34	255. 3	4. 42	11. 29	15. 71	28. 13	71. 87	21. 74	391. 71
24	79. 92	20. 08	251. 3	4. 44	11. 15	15. 59	28. 48	71. 52	22. 09	397. 95
25	80. 18	19. 82	247. 2	4. 45	11. 00	15. 45	28. 80	71. 20	22. 45	404. 49
26	80. 44	19. 56	243. 1	4. 46	10. 86	15. 32	29. 11	70. 89	22. 83	411. 33
27	80. 71	19. 29	239. 0	4. 48	10. 71	15. 19	29. 49	70. 51	23. 23	418. 47
28	80. 99	19. 01	234. 7	4. 50	10. 55	15. 05	29. 90	70. 10	23. 64	425. 91
29	81. 26	18. 74	230. 6	4. 51	10. 40	14. 91	30. 25	69. 75	24. 07	433. 65
30	81. 54	18. 46	226. 4	4. 53	10. 25	14. 78	30. 65	69. 35	24. 52	441. 70
31	81. 82	18. 18	222. 2	4. 54	10. 09	14. 63	31. 03	68. 97	24. 98	450. 04
32	82. 10	17. 90	218. 0	4. 56	9. 94	14. 50	31. 45	68. 55	25. 46	458. 68
33	82. 38	17. 62	213. 9	4. 57	9. 78	14. 35	31. 85	68. 15	25. 96	467. 62
34	82. 66	17. 34	209. 8	4. 59	9. 62	14. 21	32. 30	67. 70	26. 47	476. 87
35	82. 95	17. 05	205. 5	4. 60	9. 46	14. 06	32. 69	67. 31	27. 00	486. 41
36	83. 23	16. 77	201. 5	4. 62	9. 31	13. 93	33. 17	66. 83	27. 55	496. 25
37	83. 51	16. 49	197. 5	4. 64	9. 15	13. 79	33. 65	66. 35	28. 11	506. 40
38	83. 79	16. 21	193. 5	4. 65	9. 00	13. 65	34. 07	65. 93	28. 69	516. 84
39	84. 07	15. 93	189. 5	4. 67	8. 84	13. 51	34. 57	65. 43	29. 28	527. 58
40	84. 34	15. 66	185. 7	4. 68	8. 69	13. 37	35. 00	65. 00	29. 90	538. 63
41	84. 61	15. 39	181. 9	4. 70	8. 54	13. 24	35. 50	64. 50	30. 53	549. 97
42	84. 89	15. 11	178. 0	4. 71	8. 39	13. 10	35. 95	64. 05	31. 17	561. 62
43	85. 15	14. 85	174. 4	4. 73	8. 24	12. 97	36. 47	63. 53	31. 84	573. 56
44	85. 42	14. 58	170. 7	4. 74	8. 09	12. 83	36. 94	63. 06	32. 52	585. 81

TABLE 138.—*Solubility of levulose in water*—Continued

Temperature	Basis of computation									
	Composition		Water to 1 kg. levulose	Number of molecular weights in 1 kg of solution			Mole fraction		Concentration of levulose in—	
	Levulose	Water		Levulose	Water	Total	Levulose	Water	1 kg of water	100 g of water
°C	*Percent*	*Percent*	*g*	*Moles*	*Moles*	*Moles*	*Percent*	*Percent*	*Moles*	*g*
45	85. 68	14. 32	167. 1	4. 76	7. 95	12. 71	37. 45	62. 55	33. 21	598. 35
46	85. 94	14. 06	163. 6	4. 77	7. 80	12. 57	37. 95	62. 05	33. 93	611. 20
47	86. 19	13. 81	160. 2	4. 78	7. 67	12. 45	38. 39	61. 61	34. 66	624. 34
48	86. 45	13. 55	156. 7	4. 80	7. 52	12. 32	38. 96	61. 04	35. 40	637. 79
49	86. 69	13. 31	153. 5	4. 81	7. 39	12. 20	39. 43	60. 57	36. 16	651. 53
50	86. 94	13. 06	150. 2	4. 83	7. 25	12. 08	39. 98	60. 02	36. 94	665. 58
51	87. 18	12. 82	147. 1	4. 84	7. 12	11. 96	40. 47	59. 53	37. 74	679. 93
52	87. 41	12. 59	144. 0	4. 85	6. 99	11. 84	40. 96	59. 04	38. 55	694. 57
53	87. 65	12. 35	140. 9	4. 87	6. 86	11. 73	41. 52	58. 48	39. 38	709. 52
54	87. 88	12. 12	137. 9	4. 88	6. 73	11. 61	42. 03	57. 97	40. 23	724. 77
55	88. 10	11. 90	135. 1	4. 89	6. 61	11. 50	42. 52	57. 48	41. 09	740. 32

TABLE 139.—*Concentration*

[Concentrations of supersaturated solutions of levulose at various percentages of "oversaturation", e_t, where given solution, and c_t stands for the weight of levulose required to saturate unit weight of water at temp- oversaturation at any specified temperature for a given solution is the weight deviation of its dissolved of saturation requirement at the specified temperature. In the last column but one, this value is indicated value is expressed as a percentage of the total weight of levulose in unit weight of water, at whatever To facilitate intercalculation and interpolation, some of the data are presented in five significant digits.

Over saturation, e_t	Temperature, t	Supersaturation	Levulose	Water to 1 kg of levulose	Number of formula weights in 1 kg of solution		
					Levulose	Water	Total
	° C	k	%	g	Moles	Moles	Moles
1. 5	20	1. 003	79. 18	262. 9	4. 40	11. 55	15. 95
	25	1. 003	80. 41	243. 6	4. 46	10. 87	15. 33
	30	1. 003	81. 76	223. 0	4. 54	10. 12	14. 66
	35	1. 003	83. 16	202. 5	4. 62	9. 35	13. 97
	40	1. 002	84. 54	182. 9	4. 69	8. 58	13. 27
	45	1. 002	85. 86	164. 7	4. 77	7. 85	12. 62
	50	1. 002	87. 11	148. 0	4. 84	7. 16	12. 00
	55	1. 002	88. 25	133. 1	4. 90	6. 52	11. 42
3. 0	20	1. 006	79. 42	259. 1	4. 41	11. 42	15. 83
	25	1. 006	80. 64	240. 0	4. 48	10. 74	15. 22
	30	1. 005	81. 98	219. 8	4. 55	10. 00	14. 55
	35	1. 005	83. 36	199. 6	4. 63	9. 24	13. 87
	40	1. 005	84. 73	180. 2	4. 70	8. 48	13. 18
	45	1. 004	86. 04	162. 3	4. 78	7. 75	12. 53
	50	1. 004	87. 27	145. 9	4. 84	7. 07	11. 91
	55	1. 003	88. 41	131. 1	4. 91	6. 44	11. 35
4. 5	20	1. 009	79. 66	255. 3	4. 42	11. 29	15. 71
	25	1. 009	80. 87	236. 6	4. 49	10. 62	15. 11
	30	1. 008	82. 19	216. 6	4. 56	9. 88	14. 44
	35	1. 007	83. 56	196. 7	4. 64	9. 12	13. 76
	40	1. 007	84. 92	177. 6	4. 71	8. 37	13. 08
	45	1. 006	86. 21	159. 9	4. 79	7. 65	12. 44
	50	1. 006	87. 43	143. 8	4. 85	6. 98	11. 83
	55	1. 005	88. 55	129. 3	4. 92	6. 35	11. 27
6. 0	20	1. 012	79. 89	251. 7	4. 43	11. 16	15. 59
	25	1. 011	81. 09	233. 2	4. 50	10. 50	15. 00
	30	1. 011	82. 40	213. 6	4. 57	9 77	14. 34
	35	1. 010	83. 76	194. 0	4. 65	9. 02	13. 67
	40	1. 009	85. 10	175. 1	4. 72	8. 27	12. 99
	45	1. 008	86. 38	157. 7	4. 79	7. 56	12. 35
	50	1. 007	87. 59	141. 7	4. 86	6. 89	11. 75
	55	1. 007	88. 70	127. 4	4. 92	6. 27	11. 19

data for levulose in water

$e_t=100(c'-c_t)/c_t$, in which c' stands for the weight of levulose dissolved in unit weight of water in the erature, t, according to the equation $c_t=0.150103t^2-0.814t+331.023$, as listed in table 138. The index of levulose contents per unit weight of water, regardless of existing temperature, expressed as a percentage for the specified temperature of 20° C; in the last column, headed "y_{20}", (hypothetical yield at 20°), this temperature, instead of as a percentage of the weight which would exactly saturate the water at 20° C. In practical application only the first three or four digits should be used]

Over saturation, e_t	Mole fraction		Concentration of levulose in—				Oversaturation	
			1 kg of water	100 g of water				
				Total	Excess at—			
	Levulose	Water			t	20°	e_{20}	y_{20}
	%	%	M	g	g	g	%	%
1.5	27.56	72.44	21.11	380.40	5.62	5.62	1.50	1.48
	29.11	70.89	22.79	410.56	6.07	35.78	9.55	8.71
	30.96	69.04	24.89	448.33	6.63	73.55	19.62	16.41
	33.05	66.95	24.40	493.71	7.30	118.93	31.73	24.09
	35.35	64.65	30.35	546.71	8.08	171.93	45.87	31.45
	37.79	62.21	33.71	607.33	8.98	232.55	62.05	38.29
	40.32	59.68	37.50	675.56	9.98	300.78	80.26	44.52
	42.90	57.10	41.71	751.41	11.10	376.63	100.49	50.12
3.0	27.85	72.15	21.43	386.02	11.24	11.24	3.00	2.91
	29.41	70.59	23.13	416.62	12.13	41.84	11.16	10.04
	31.27	68.73	25.25	454.95	13.25	80.17	21.39	17.62
	33.38	66.62	27.81	501.00	14.59	126.22	33.68	25.19
	35.68	64.32	30.79	554.79	16.16	180.01	48.03	32.45
	38.13	61.87	34.21	616.30	17.95	241.52	64.44	39.19
	40.67	59.33	38.05	685.55	19.97	310.77	82.92	45.33
	43.26	56.74	42.33	762.52	22.21	387.74	103.46	50.85
4.5	28.14	71.86	21.74	391.65	16.87	16.87	4.50	4.31
	29.71	70.29	23.46	422.69	18.20	47.91	12.78	11.33
	31.58	68.42	25.62	461.58	19.88	86.80	23.16	18.80
	33.70	66.30	28.21	508.30	21.89	133.52	35.63	26.27
	36.02	63.98	31.24	562.87	24.24	188.09	50.19	33.42
	38.47	61.53	34.71	625.28	26.93	250.50	66.84	40.06
	41.02	58.98	38.61	695.53	29.95	320.75	85.58	46.12
	43.62	56.38	42.94	773.62	33.31	398.84	106.42	51.56
6.0	28.43	71.57	22.05	397.27	22.49	22.49	6.00	5.66
	30.01	69.99	23.80	428.76	24.27	53.98	14.40	12.59
	31.89	68.11	25.99	468.20	26.50	93.42	24.93	19.95
	34.02	65.98	28.62	515.59	29.18	140.81	37.57	27.31
	36.34	63.66	31.69	570.95	32.32	196.17	52.34	34.36
	38.81	61.19	35.21	634.25	35.90	256.47	68.43	40.44
	41.37	58.63	39.16	705.51	39.93	330.73	88.25	46.88
	43.97	56.03	43.56	784.73	44.42	409.95	109.38	52.24

TABLE 139.—*Concentration data*

Over saturation, e_t	Temperature, t	Supersaturation	Levulose	Water to 1 kg of levulose	Number of formula weights in 1 kg of solution		
					Levulose	Water	Total
	° *C*	*k*	%	*g*	*Moles*	*Moles*	*Moles*
7.5	20	1.015	80.11	248.2	4.45	11.04	15.49
	25	1.014	81.30	230.0	4.51	10.38	14.89
	30	1.013	82.60	210.6	4.58	9.66	14.24
	35	1.012	83.95	191.2	4.66	8.91	13.57
	40	1.011	85.27	172.7	4.73	8.17	12.90
	45	1.010	86.55	155.5	4.80	7.47	12.27
	50	1.009	87.74	139.8	4.87	6.81	11.68
	55	1.008	88.84	125.7	4.93	6.20	11.13
9.0	20	1.018	80.33	244.8	4.46	10.92	15.38
	25	1.017	81.51	226.8	4.52	10.26	14.78
	30	1.015	82.80	207.7	4.60	9.55	14.15
	35	1.014	84.13	188.6	4.67	8.81	13.48
	40	1.013	85.45	170.3	4.74	8.08	12.82
	45	1.012	86.71	153.3	4.81	7.38	12.19
	50	1.011	87.89	137.8	4.88	6.72	11.60
	55	1.010	88.97	123.9	4.94	6.12	11.06
10.5	20	1.020	80.55	241.5	4.47	10.80	15.27
	25	1.019	81.72	223.7	4.54	10.15	14.69
	30	1.018	83.00	204.9	4.61	9.44	14.05
	35	1.016	84.31	186.1	4.68	8.71	13.39
	40	1.015	85.62	168.0	4.75	7.98	12.73
	45	1.014	86.86	151.2	4.82	7.29	12.11
	50	1.013	88.03	136.0	4.89	6.64	11.53
	55	1.011	89.11	122.2	4.95	6.05	11.00
12.0	20	1.023	80.76	238.2	4.48	10.68	15.16
	25	1.022	81.92	220.7	4.55	10.04	14.59
	30	1.020	83.18	202.1	4.62	9.33	13.95
	35	1.019	84.49	183.6	4.69	8.61	13.30
	40	1.017	85.78	165.8	4.76	7.89	12.65
	45	1.016	87.02	149.2	4.83	7.21	12.04
	50	1.014	88.17	134.1	4.89	6.57	11.46
	55	1.013	89.24	120.6	4.95	5.97	10.92
13.5	20	1.026	80.97	235.1	4.49	10.56	15.05
	25	1.024	82.11	217.8	4.56	9.93	14.49
	30	1.022	83.37	199.5	4.63	9.23	13.86
	35	1.021	84.66	181.1	4.70	8.51	13.21
	40	1.019	85.94	163.6	4.77	7.80	12.57
	45	1.017	87.17	147.2	4.84	7.12	11.96
	50	1.016	88.31	132.4	4.90	6.49	11.39
	55	1.014	89.36	119.0	4.96	5.90	10.86

for levulose in water—Continued

Over saturation, e_t	Mole fraction		Concentration of levulose in—				Oversaturation	
			1 kg of water	100 g of water				
				Total	Excess at—			
	Levulose	Water			t	20°	e_{20}	y_{20}
	%	%	M	g	g	g	%	%
7.5	28.72	71.28	22.36	402.89	28.11	28.11	7.50	6.98
	30.31	69.69	24.14	434.83	30.34	60.05	16.02	13.81
	32.20	67.80	26.36	474.83	33.13	100.05	26.69	21.07
	34.34	65.66	29.02	522.89	36.48	148.11	39.52	28.33
	36.67	63.33	32.14	579.03	40.40	204.25	54.50	35.27
	39.14	60.86	35.70	643.23	44.88	268.45	71.63	41.73
	41.71	58.29	39.72	715.50	49.92	340.72	90.91	47.62
	44.32	55.68	44.17	795.83	55.52	421.05	112.35	52.91
9.0	29.00	71.00	22.68	408.51	33.73	33.73	9.00	8.26
	30.60	69.40	24.47	440.89	36.40	66.11	17.64	14.99
	32.50	67.50	26.72	481.45	39.75	106.67	28.46	22.16
	34.65	65.35	29.43	530.19	43.78	155.41	41.47	29.31
	36.99	63.01	32.59	587.11	48.48	212.33	56.65	36.17
	39.48	60.52	36.20	652.20	53.85	277.42	74.02	42.54
	42.05	57.95	40.27	725.48	59.90	350.70	93.57	48.34
	44.66	55.34	44.79	806.94	66.63	432.16	115.31	53.56
10.5	29.29	70.71	22.99	414.13	39.35	39.35	10.50	9.50
	30.89	69.11	24.81	446.96	42.47	72.18	19.26	16.15
	32.80	67.20	27.09	488.08	46.38	113.30	30.23	23.21
	34.96	65.04	29.83	537.48	51.07	162.70	43.41	30.27
	37.31	62.69	33.04	595.19	56.56	220.41	58.81	37.03
	39.80	60.20	36.70	661.18	62.83	286.40	76.42	43.32
	42.38	57.62	40.82	735.47	69.89	360.69	96.24	49.04
	45.00	55.00	45.41	818.04	77.73	443.26	118.27	54.19
12.0	29.57	70.43	23.30	419.75	44.97	44.97	12.00	10.71
	31.18	68.82	25.15	453.03	48.54	78.25	20.88	17.27
	33.10	66.90	27.46	494.70	53.00	119.92	32.00	24.24
	35.27	64.73	30.24	544.78	58.37	170.00	45.36	31.21
	37.63	62.37	33.49	603.27	64.64	228.54	60.98	37.88
	40.13	59.87	37.20	670.15	71.80	295.37	78.81	44.08
	42.71	57.29	41.38	745.45	79.87	370.67	98.90	49.72
	45.33	54.67	46.02	829.15	88.84	454.37	121.24	54.80
13.5	29.84	70.16	23.61	425.38	50.60	50.60	13.50	11.90
	31.47	68.53	25.48	459.10	54.61	84.32	22.50	18.37
	33.39	66.61	27.83	501.33	59.63	126.55	33.77	25.24
	35.57	64.43	30.64	552.08	65.67	117.30	47.31	32.11
	37.94	62.06	33.93	611.35	72.72	236.57	63.12	38.70
	40.45	59.55	37.70	679.13	80.78	304.35	81.21	44.81
	43.03	56.97	41.93	755.43	89.85	380.65	101.57	50.39
	45.66	54.34	46.64	840.25	99.94	465.47	124.20	55.40

323414°—42——45

TABLE 139.—*Concentration data*

Over saturation, *e;*	Temperature, *t*	Supersaturation	Levulose	Water to 1 kg of levulose	Number of formula weights in 1 kg of solution		
					Levulose	Water	Total
	° *C*	*k*	%	*g*	*Moles*	*Moles*	*Moles*
15. 0	20	1. 028	81. 17	232. 0	4. 51	10. 45	14. 96
	25	1. 027	82. 31	215. 0	4. 57	9. 82	14. 39
	30	1. 025	83. 55	196. 9	4. 64	9. 13	13. 77
	35	1. 023	84. 83	178. 8	4. 71	8. 42	13. 13
	40	1. 021	86. 10	161. 4	4. 78	7. 72	12. 50
	45	1. 019	87. 31	145. 3	4. 85	7. 04	11. 89
	50	1. 017	88. 44	130. 6	4. 91	6. 41	11. 32
	55	1. 016	89. 49	117. 5	4. 97	5. 83	10. 80
16. 5	20	1. 031	81. 36	229. 0	4. 52	10. 34	14. 86
	25	1. 029	82. 49	212. 2	4. 58	9. 72	14. 30
	30	1. 027	83. 73	194. 3	4. 65	9. 03	13. 68
	35	1. 025	85. 00	176. 5	4. 72	8. 33	13. 05
	40	1. 023	86. 25	159. 4	4. 79	7. 63	12. 42
	45	1. 021	87. 45	143. 5	4. 85	6. 97	11. 82
	50	1. 019	88. 58	129. 0	4. 92	6. 34	11. 26
	55	1. 017	89. 61	115. 9	4. 97	5. 77	10. 74
18. 0	20	1. 033	81. 56	226. 1	4. 53	10. 24	14. 77
	25	1. 031	82. 68	209. 5	4. 59	9. 61	14. 20
	30	1. 029	83. 90	191. 9	4. 66	8. 94	13. 60
	35	1. 027	85. 16	174. 2	4. 73	8. 24	12. 97
	40	1. 025	86. 41	157. 3	4. 80	7. 55	12. 35
	45	1. 022	87. 59	141. 6	4. 86	6. 89	11. 75
	50	1. 020	88. 71	127. 3	4. 92	6. 27	11. 19
	55	1. 018	89. 73	114. 5	4. 98	5. 70	10. 68
19. 5	20	1. 036	81. 75	223. 3	4. 54	10. 13	14. 67
	25	1. 033	82. 86	206. 9	4. 60	9. 51	14. 11
	30	1. 031	84. 07	189. 5	4. 67	8. 84	13. 51
	35	1. 029	85. 32	172. 0	4. 74	8. 15	12. 89
	40	1. 026	86. 55	155. 4	4. 80	7. 47	12. 27
	45	1. 024	87. 73	139. 9	4. 87	6. 81	11. 68
	50	1. 022	88. 83	125. 7	4. 93	6. 20	11. 13
	55	1. 020	89. 84	113. 0	4. 99	5. 64	10. 63
21. 0	20	1. 038	81. 93	220. 5	4. 55	10. 03	14. 58
	25	1. 036	83. 03	204. 3	4. 61	9. 42	14. 03
	30	1. 033	84. 24	187. 1	4. 68	8. 75	13. 43
	35	1. 031	85. 48	169. 9	4. 74	8. 06	12. 80
	40	1. 028	86. 70	153. 4	4. 81	7. 38	12. 19
	45	1. 025	87. 86	138. 1	4. 88	6. 74	11. 62
	50	1. 023	88. 95	124. 2	4. 94	6. 13	11. 07
	55	1. 021	89. 96	111. 6	4. 99	5. 57	10. 56

for levulose in water—Continued

Over saturation, *e;*	Mole fraction		Concentration of levulose in—				Oversaturation	
			1 kg of water	100 g of water				
				Total	Excess at—			
	Levulose	Water			*t*	20°	e_{20}	y_{20}
	%	%	*M*	*g*	*g*	*g*	%	%
15. 0	30. 12	69. 88	23. 92	431. 00	56. 22	56. 22	15. 00	13. 04
	31. 75	68. 25	25. 82	465. 16	60. 67	90. 38	24. 12	19. 43
	33. 69	66. 31	28. 20	507. 96	66. 26	133. 18	35. 53	26. 22
	35. 87	64. 13	31. 05	559. 37	72. 96	184. 59	49. 25	33. 00
	38. 25	61. 75	34. 38	619. 42	80. 79	244. 64	65. 28	39. 50
	40. 76	59. 24	38. 19	688. 10	89. 75	313. 32	83. 60	45. 53
	43. 36	56. 64	42. 49	765. 42	99. 84	390. 64	104. 23	51. 04
	45. 99	54. 01	47. 26	851. 36	111. 05	476. 58	127. 16	55. 98
16. 5	30. 39	69. 61	24. 24	436. 62	61. 84	61. 84	16. 50	14. 16
	32. 03	67. 97	26. 16	471. 23	66. 74	96. 45	25. 74	20. 47
	33. 98	66. 02	28. 56	514. 58	72. 88	139. 80	37. 30	27. 17
	36. 17	63. 83	31. 45	566. 67	80. 26	191. 89	51. 20	33. 86
	38. 56	61. 44	34. 83	627. 50	88. 87	252. 72	67. 43	40. 27
	41. 08	58. 92	38. 69	697. 08	98. 73	322. 30	86. 00	46. 24
	43. 68	56. 32	43. 04	775. 40	109. 82	400. 62	106. 89	51. 67
	46. 31	53. 69	47. 87	862. 46	121. 15	487. 68	130. 12	56. 55
18. 0	30. 66	69. 34	24. 55	442. 24	67. 46	67. 46	18. 00	15. 25
	32. 31	67. 69	26. 49	477. 30	72. 81	102. 52	27. 35	21. 48
	34. 26	65. 74	28. 93	521. 21	79. 51	146. 43	39. 07	28. 09
	36. 47	63. 53	31. 86	573. 96	87. 55	199. 18	53. 15	34. 70
	38. 86	61. 14	35. 28	635. 58	96. 95	260. 80	69. 59	41. 03
	41. 39	58. 61	39. 19	706. 05	107. 70	331. 27	88. 39	46. 92
	43. 99	56. 01	43. 59	785. 38	119. 80	410. 60	109. 56	52. 28
	46. 63	53. 37	48. 49	873. 57	133. 26	498. 79	133. 09	57. 10
19. 5	30. 93	69. 07	24. 86	447. 86	73. 08	73. 08	19. 50	16. 32
	32. 59	67. 41	26. 83	483. 37	78. 88	108. 59	28. 97	22. 46
	34. 55	65. 45	29. 30	527. 83	86. 13	153. 05	40. 84	29. 00
	36. 76	63. 24	32. 26	581. 26	94. 85	206. 48	55. 09	35. 53
	39. 16	60. 84	35. 73	643. 66	105. 03	268. 88	71. 75	41. 77
	41. 69	58. 31	39. 69	715. 03	116. 68	340. 25	90. 79	47. 59
	44. 30	55. 70	44. 15	795. 37	129. 79	420. 59	112. 22	52. 88
	46. 94	53. 06	49. 11	884. 67	144. 36	509. 89	136. 05	57. 64
21. 0	31. 20	68. 80	25. 17	453. 48	78. 70	78. 70	21. 00	17. 35
	32. 86	67. 14	27. 17	489. 43	84. 94	114. 65	30. 59	23. 43
	34. 83	65. 17	29. 67	534. 46	92. 76	159. 68	42. 61	29. 88
	37. 05	62. 95	32. 67	588. 56	102. 15	213. 78	57. 04	26. 32
	39. 46	60. 54	36. 18	651. 74	113. 11	276. 96	73. 90	42. 50
	42. 00	58. 00	40. 19	724. 00	125. 65	349. 22	93. 18	48. 24
	44. 61	55. 39	44. 70	805. 35	139. 77	430. 57	114. 89	53. 46
	47. 25	52. 75	49. 72	895. 78	155. 47	521. 00	139. 01	58. 16

TABLE 139.—*Concentration data*

Over saturation, *e*;	Temperature, *t*	Supersaturation	Levulose	Water to 1 kg of levulose	Number of formula weights in 1 kg of solution		
					Levulose	Water	Total
	° *C*	*k*	%	*g*	*Moles*	*Moles*	*Moles*
22. 5	20	1. 040	82. 11	217. 8	4. 56	9. 93	14. 49
	25	1. 038	83. 21	201. 8	4. 62	9. 32	13. 94
	30	1. 035	84. 40	184. 8	4. 68	8. 66	13. 34
	35	1. 032	85. 63	167. 8	4. 75	7. 98	12. 73
	40	1. 030	86. 84	151. 6	4. 82	7. 30	12. 12
	45	1. 027	87. 99	136. 4	4. 88	6. 66	11. 54
	50	1. 025	89. 08	122. 6	4. 94	6. 06	11. 00
	55	1. 022	90. 07	110. 3	5. 00	5. 51	10. 51
24. 0	20	1. 042	82. 29	215. 2	4. 57	9. 83	14. 40
	25	1. 040	83. 38	199. 4	4. 63	9. 23	13. 86
	30	1. 037	84. 56	182. 6	4. 69	8. 57	13. 26
	35	1. 034	85. 78	165. 8	4. 76	7. 89	12. 65
	40	1. 031	86. 98	149. 7	4. 83	7. 23	12. 06
	45	1. 028	88. 12	134. 8	4. 89	6. 59	11. 48
	50	1. 026	89. 19	121. 2	4. 95	6. 00	10. 95
	55	1. 023	90. 18	108. 9	5. 01	5. 45	10. 46

for levulose in water—Continued

Over saturation, *e;*	Mole fraction		Concentration of levulose in—				Oversaturation	
			1 kg of water	100 g of water				
				Total	Excess at—			
	Levulose	Water			*t*	20°	e_{20}	y_{20}
	%	%	*M*	*g*	*g*	*g*	%	%
22. 5	31. 47	68. 53	25. 48	459. 11	84. 33	84. 33	22. 50	18. 37
	33. 13	66. 87	27. 50	495. 50	91. 01	120. 72	32. 21	24. 36
	35. 11	64. 89	30. 03	541. 08	99. 38	166. 30	44. 37	30. 74
	37. 34	62. 66	33. 07	595. 85	109. 44	221. 07	58. 99	37. 10
	39. 75	60. 25	36. 62	659. 82	121. 19	285. 04	76. 06	43. 20
	42. 30	57. 70	40. 69	732. 98	134. 63	358. 20	95. 58	48. 87
	44. 91	55. 09	45. 26	815. 34	149. 76	440. 56	117. 55	54. 03
	47. 56	52. 44	50. 34	906. 88	166. 57	532. 10	141. 98	58. 67
24. 0	31. 73	68. 27	25. 80	464. 73	89. 95	89. 95	24. 00	19. 36
	33. 40	66. 60	27. 84	501. 57	97. 08	126. 79	33. 83	25. 58
	35. 39	64. 61	30. 40	547. 71	106. 01	172. 93	46. 14	31. 57
	37. 62	62. 38	33. 48	603. 15	116. 74	228. 37	60. 93	37. 86
	40. 05	59. 95	37. 07	667. 90	129. 27	293. 12	78. 21	43. 89
	42. 59	57. 41	41. 18	741. 95	143. 60	367. 17	97. 97	49. 49
	45. 22	54. 78	45. 81	825. 32	159. 74	450. 54	120. 21	54. 59
	47. 86	52. 14	50. 95	917. 98	177. 67	543. 20	144. 94	59. 17

TABLE 140.—*Solubility of lactose in water*

[The respective solid phases are in equilibrium with their saturated solutions in which the mutarotation is complete]

Temperature	Lactose in saturated solution [a]	Observer [b]
SOLID PHASE, α-LACTOSE HYDRATE		
° C	*Percent*	
0	10. 6	H
15	14. 4	H
21. 5	16. 7	S
25	17. 8	H
28	19. 4	S
38	23. 5	S
39	24. 0	H
48 [c]	29. 6	S
49	29. 7	H
57. 0 [c]	35. 9	S
57. 1	34. 9	G
63. 9	39. 1	G
64. 0	39. 7	H
65. 0 [c]	43. 5	S
73. 5	45. 8	G
74. 0	46. 2	H
79. 1	49. 6	G
87. 2	55. 1	G
88. 2	56. 0	G
89. 0 [c]	58. 1	H
SOLID PHASE, β-LACTOSE (ANHYDROUS)		
100. 0	60. 7	H
107. 0	63. 9	G
121. 5	69. 4	G
133. 6	73. 2	G
138. 8	75. 2	G
158. 8	81. 1	G
178. 8	86. 7	G

[a] Referred to anhydrous lactose.
[b] H=C. S. Hudson; S=E. Saillard; G=J. Gillis.
[c] These temperatures deviated somewhat from a plotted curve.

TABLE 141.—*Approximate composition of invert-sugar solutions saturated with respect to dextrose at various temperatures* (computed)

Temperature	Dextrose in water	Composition of invert sugar solutions saturated with dextrose	Invert sugar to 100 g of water
°C	*Percent*	*Percent*	*g*
0	35. 0	50. 8	103. 3
10. 0	40. 8	56. 6	130. 4
15. 0	44. 0	59. 8	148. 7
20. 0	47. 2	62. 6	167. 4
25. 0	50. 80	66. 2	195. 8
30. 0	54. 64	69. 7	230. 0
35. 0	58. 02	72. 2	259. 7
40. 0	61. 87	74. 8	296. 8
45. 0	65. 71	78. 0	354. 5
50. 0	70. 91	81. 9	452. 5

TABLE 142.—*The system: Dextrose, levulose, and water, at 30° C, with hydrated dextrose as the solid phase*

Dextrose by weight	Levulose by weight	$d\,^{30°}_{4°}$	Dextrose to 100 g of water	Levulose to 100 g of water	Total sugar
Percent	*Percent*		*g*	*g*	*Percent*
54. 64	0. 00	----------	120. 46	0	54. 64
49. 34	8. 94	1. 2639	118. 26	21. 43	58. 28
49. 32	8. 94	1. 2650	118. 16	21. 42	58. 26
45. 97	14. 50	1. 2779	116. 27	36. 68	60. 47
41. 01	23. 23	1. 3000	114. 68	64. 96	64. 24
35. 76	33. 09	1. 3286	114. 83	106. 23	68. 85
34. 48	35. 69	1. 3359	115. 59	119. 23	70. 17
33. 67	37. 10	1. 3408	115. 19	126. 92	70. 77
32. 55	39. 39	1. 3480	116. 00	140. 38	71. 94

TABLE 143.—*Influence of invert sugar on the solubility of sucrose*

[All solutions are saturated with respect to sucrose]

Invert sugar to 100 g of water	Sucrose in 100 g of water at—		
	23.15° C	30° C	50° C
g	*g*	*g*	*g*
0	208. 6	213. 6	260. 4
20	198. 8	206. 7	252. 1
40	190. 8	200. 1	245. 0
80	177. 2	188. 1	233. 2
160	156. 0	167. 3	213. 9
200	----------	159. 3	207. 9
300	----------	147. 3	196. 0
400	----------	140. 4	188. 5

TABLE 144.—*Composition of solutions of maximum solubility at various temperatures (computed)*

Temperature	Sucrose	Invert sugar	Water	Sucrose to 100 g of water	Invert sugar to 100 g of water	Total sugar to 100 g of water	Sucrose alone to 100 g of water
°*C*	%	%	%	*g*	*g*	*g*	*g*
0	43. 7	27. 2	29. 1	150. 2	93. 5	243. 7	179. 2
10	40. 9	31. 8	27. 3	149. 8	116. 5	266. 3	190. 5
15	39. 1	34. 8	26. 1	149. 8	133. 4	283. 2	197. 0
23. 15	36. 3	39. 9	23. 8	152. 5	167. 6	319. 1	208. 5
30	33. 6	45. 4	21. 0	160. 0	216. 2	376. 2	213. 6
40	31. 1	50. 7	18. 2	170. 9	278. 6	449. 5	238. 1
50	27. 7	58. 0	14. 3	193. 7	405. 6	599. 3	260. 4

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TABLE 145.—*Elevation of the boiling point*[a] *of sucrose solutions above that of water at various pressures*

Solids per 100 g. of water	Brix	Vapor pressure, pounds per square inch						
		2.8886	3.6269	4.5193	5.5908	6.8688	8.3837	10.168
		Vapor pressure, millimeters of mercury						
		149.38	187.56	233.71	289.13	355.22	433.56	525.84
		Boiling point of water, degrees centigrade						
		60	65	70	75	80	85	90
		Elevation, degrees centigrade, above the boiling point of water						
		100-PERCENT PURITY						
g								
50	33. 33	0. 56	0. 58	0. 61	0. 63	0. 65	0. 67	0. 69
100	50. 00	1. 37	1. 41	1. 46	1. 52	1. 57	1. 62	1. 68
150	60. 00	2. 27	2. 35	2. 44	2. 52	2. 61	2. 70	2. 79
200	66. 67	3. 24	3. 36	3. 48	3. 60	3. 72	3. 85	3. 98
250	71. 43	4. 25	4. 40	4. 56	4. 71	4. 88	5. 04	5. 22
300	75. 00	5. 25	5. 44	5. 63	5. 82	6. 02	6. 23	6. 44
350	77. 78	6. 23	6. 46	6. 69	6. 92	7. 16	7. 41	7. 66
400	80. 00	-------	-------	-------	-------	8. 27	8. 55	8. 84
450	81. 82	-------	-------	-------	-------	-------	9. 64	9. 97
500	83. 33	-------	-------	-------	-------	-------	-------	-------
550	84. 62	-------	-------	-------	-------	-------	-------	-------
600	85. 71	-------	-------	-------	-------	-------	-------	-------
650	86. 67	-------	-------	-------	-------	-------	-------	-------
700	87. 50	-------	-------	-------	-------	-------	-------	-------
750	88. 24	-------	-------	-------	-------	-------	-------	-------
800	88. 89	-------	-------	-------	-------	-------	-------	-------
850	89. 47	-------	-------	-------	-------	-------	-------	-------
900	90. 00	-------	-------	-------	-------	-------	-------	-------
950	90. 48	-------	-------	-------	-------	-------	-------	-------
1,000	90. 91	-------	-------	-------	-------	-------	-------	-------
1,050	91. 30	-------	-------	-------	-------	-------	-------	-------
1,100	91. 67	-------	-------	-------	-------	-------	-------	-------
1,150	92. 00	-------	-------	-------	-------	-------	-------	-------
1,200	92. 31	-------	-------	-------	-------	-------	-------	-------
1,250	92. 59	-------	-------	-------	-------	-------	-------	-------
1,300	92. 86	-------	-------	-------	-------	-------	-------	-------
1,350	93. 10	-------	-------	-------	-------	-------	-------	-------
1,400	93. 33	-------	-------	-------	-------	-------	-------	-------
1,450	93. 55	-------	-------	-------	-------	-------	-------	-------
1,500	93. 75	-------	-------	-------	-------	-------	-------	-------
1,550	93. 94	-------	-------	-------	-------	-------	-------	-------
1,600	94. 12	-------	-------	-------	-------	-------	-------	-------

[a] To find the boiling point of a solution of sugar and water, add the boiling point elevation to the boiling point of water at the top of the column.

TABLE 145.—*Elevation of the boiling point*[a] *of sucrose solutions above that of water at various vapor pressures*—Continued

Solids per 100 g. of water	Vapor pressure, pounds per square inch							
	12.260	14.696	17.520	20.779	24.519	28.795	33.661	39.177
	Vapor pressure, millimeters of mercury							
	634.02	760.00	906.04	1074.58	1267.99	1489.12	1740.77	2026.03
	Boiling point of water, degrees centigrade							
	95	100	105	110	115	120	125	130
	Elevation, degrees centigrade, above the boiling point of water							
	100-PERCENT PURITY							
g								
50	0. 72	0. 74	0. 76	0. 79	0. 82	0. 84	0. 87	0. 90
100	1. 73	1. 79	1. 85	1. 91	1. 97	2. 04	2. 10	2. 17
150	2. 88	2. 98	3. 08	3. 18	3. 28	3. 39	3. 50	3. 61
200	4. 11	4. 25	4. 39	4. 53	4. 68	4. 83	4. 99	5. 15
250	5. 39	5. 57	5. 75	5. 94	6. 14	6. 34	6. 54	6. 75
300	6. 66	6. 88	7. 11	7. 34	7. 58	7. 83	8. 08	8. 34
350	7. 92	8. 18	8. 45	8. 73	9. 01	9. 30	9. 60	9. 91
400	9. 14	9. 44	9. 75	10. 07	10. 40	10. 74	11. 08	11. 44
450	10. 31	10. 65	11. 00	11. 36	11. 73	12. 11	12. 50	12. 90
500	--------	11. 81	12. 20	12. 60	13. 01	13. 43	13. 87	14. 31
550	--------	12. 93	13. 36	13. 80	14. 25	14. 71	15. 18	15. 67
600	--------	13. 98	14. 44	14. 92	15. 40	15. 90	16. 42	16. 94
650	--------	14. 98	15. 47	15. 98	16. 50	17. 04	17. 59	18. 15
700	--------	15. 93	16. 46	17. 00	17. 55	18. 12	18. 71	-------
750	--------	16. 84	17. 40	17. 97	18. 55	19. 16	19. 77	-------
800	--------	17. 69	18. 27	18. 88	19. 49	20. 12	20. 77	-------
850	--------	18. 51	19. 12	19. 75	20. 39	21. 06	21. 73	-------
900	--------	19. 27	19. 91	20. 56	21. 23	21. 92	22. 63	-------
950	--------	20. 01	20. 67	21. 35	22. 05	22. 76	23. 50	-------
1,000	--------	20. 70	21. 38	22. 09	22. 81	23. 55	24. 31	-------
1,050	--------	21. 36	22. 06	22. 79	23. 53	24. 30	25. 08	-------
1,100	--------	21. 99	22. 72	23. 46	24. 23	25. 01	25. 82	-------
1,150	--------	22. 58	23. 33	24. 09	24. 88	25. 68	26. 51	-------
1,200	--------	23. 16	23. 92	24. 71	25. 52	26. 34	27. 19	-------
1,250	--------	23. 70	24. 48	25. 29	26. 11	26. 96	27. 83	-------
1,300	--------	24. 22	25. 02	25. 84	26. 69	27. 55	28. 44	-------
1,350	--------	24. 71	25. 53	26. 37	27. 23	28. 11	29. 01	-------
1,400	--------	25. 18	26. 01	26. 87	27. 74	28. 64	29. 57	-------
1,450	--------	25. 64	26. 49	27. 36	28. 25	29. 17	30. 11	-------
1,500	--------	26. 07	26. 93	27. 82	28. 72	29. 65	30. 61	-------
1,550	--------	26. 49	27. 36	28. 26	29. 19	30. 13	31. 10	-------
1,600	--------	26. 88	27. 77	28. 68	29. 62	30. 58	31. 56	-------

Example.—Required: the boiling point, under a pressure of 4.5 lb./in.^{2} of a 92 Brix, 90 purity, sucrose solution. Boiling point $=70°+19.58°=89.58°$ C.

TABLE 145.—*Elevation of the boiling point*[a] *of sucrose solutions above that of water at various vapor pressures*—Continued

Solids per 100 g. of water	Brix	Vapor pressure, pounds per square inch						
		2.8886	3.6269	4.5193	5.5908	6.8688	8.3837	10.168
		Vapor pressure, millimeters of mercury						
		149.38	187.56	233.71	289.13	355.22	433.56	525.84
		Boiling point of water, degrees centigrade						
		60	65	70	75	80	85	90
		Elevation, degrees centigrade, above the boiling point of water						
		90-PERCENT PURITY [b]						
50	33. 33	0. 66	0. 68	0. 70	0. 73	0. 75	0. 78	0. 80
100	50. 00	1. 61	1. 67	1. 73	1. 79	1. 85	1. 91	1. 97
150	60. 00	2. 64	2. 73	2. 83	2. 93	3. 03	3. 13	3. 24
200	66. 67	3. 70	3. 83	3. 97	4. 11	4. 25	4. 39	4. 54
250	71. 43	4. 78	4. 95	5. 12	5. 30	5. 48	5. 67	5. 85
300	75. 00	5. 84	6. 04	6. 26	6. 47	6. 70	6. 93	7. 16
350	77. 78	6. 88	7. 13	7. 38	7. 63	7. 90	8. 17	8. 44
400	80. 00	7. 88	8. 16	8. 45	8. 74	9. 05	9. 35	9. 66
450	81. 82	8. 85	9. 17	9. 49	9. 82	10. 16	10. 50	10. 85
500	83. 33	9. 77	10. 12	10. 48	10. 84	11. 22	11. 60	11. 99
550	84. 62	10. 65	11. 03	11. 42	11. 82	12. 22	12. 64	13. 07
600	85. 71	11. 49	11. 90	12. 32	12. 75	13. 19	13. 64	14. 10
650	86. 67	--------	12. 71	13. 16	13. 62	14. 09	14. 57	15. 07
700	87. 50	--------	13. 49	13. 97	14. 46	14. 96	15. 47	15. 99
750	88. 24	--------	14. 23	14. 73	15. 24	15. 77	16. 31	16. 86
800	88. 89	--------	14. 93	15. 46	16. 00	16. 55	17. 12	17. 70
850	89. 47	--------	15. 60	16. 15	16. 71	17. 29	17. 88	18. 49
900	90. 00	--------	16. 22	16. 79	17. 38	17. 98	18. 59	19. 22
950	90. 48	--------	16. 82	17. 41	18. 02	18. 64	19. 28	19. 93
1,000	90. 91	--------	17. 38	17. 99	18. 62	19. 27	19. 92	20. 60
1,050	91. 30	--------	17. 92	18. 55	19. 20	19. 86	20. 54	21. 24
1,100	91. 67	--------	18. 43	19. 08	19. 75	20. 43	21. 13	21. 84
1,150	92. 00	--------	18. 91	19. 58	20. 26	20. 96	21. 68	22. 42
1,200	92. 31	--------	19. 39	20. 07	20. 77	21. 49	22. 22	22. 98
1,250	92. 59	--------	19. 82	20. 52	21. 24	21. 97	22. 72	23. 50
1,300	92. 86	--------	20. 25	20. 96	21. 69	22. 44	23. 21	24. 00
1,350	93. 10	--------	20. 65	21. 38	22. 12	22. 89	23. 67	24. 47
1,400	93. 33	--------	21. 04	21. 78	22. 54	23. 32	24. 12	24. 93
1,450	93. 55	--------	21. 40	22. 16	22. 93	23. 72	24. 53	25. 36
1,500	93. 75	--------	21. 76	22. 52	23. 31	24. 12	24. 94	25. 79
1,550	93. 94	--------	22. 10	22. 88	23. 67	24. 49	25. 33	26. 19
1,600	94. 12	--------	22. 43	23. 22	24. 03	24. 86	25. 71	26. 58

[a] See footnote *a*, p. 694–5.
[b] Values given in the table for impure solutions are based on determinations made on product in which the impurity was beet molasses.

TABLE 145.—*Elevation of the boiling point* [a] *of sucrose solutions above that of water at various vapor pressures*—Continued

Solids per 100 g. of water	Vapor pressure, pounds per square inch							
	12.260	14.696	17.520	20.779	24.519	28.795	33.661	39.177
	Vapor pressure, millimeters of mercury							
	634.02	760.00	906.04	1074.58	1267.99	1489.12	1740.77	2026.03
	Boiling point of water, degrees centigrade							
	95	100	105	110	115	120	125	130
	Elevation, degrees centigrade, above the boiling point of water							
	90-PERCENT PURITY [b]							
50	0. 83	0. 86	0. 89	0. 92	0. 95	0. 98	1. 01	1. 04
100	2. 04	2. 11	2. 18	2. 25	2. 32	2. 40	2. 48	2. 56
150	3. 35	3. 46	3. 57	3. 69	3. 81	3. 94	4. 06	4. 19
200	4. 69	4. 85	5. 01	5. 17	5. 34	5. 52	5. 69	5. 88
250	6. 06	6. 26	6. 47	6. 68	6. 90	7. 12	7. 35	7. 59
300	7. 40	7. 65	7. 90	8. 16	8. 43	8. 70	8. 98	9. 27
350	8. 73	9. 02	9. 32	9. 62	9. 94	10. 26	10. 59	10. 93
400	10. 00	10. 33	10. 67	11. 02	11. 38	11. 75	12. 13	12. 52
450	11. 23	11. 60	11. 98	12. 38	12. 78	13. 20	13. 62	14. 06
500	12. 40	12. 81	13. 23	13. 67	14. 11	14. 57	15. 04	15. 52
550	13. 51	13. 96	14. 42	14. 90	15. 38	15. 88	16. 39	16. 92
600	14. 58	15. 06	15. 56	16. 07	16. 59	17. 13	17. 68	18. 25
650	15. 57	16. 09	16. 62	17. 17	17. 73	18. 30	18. 89	19. 50
700	16. 53	17. 08	17. 64	18. 22	18. 82	19. 43	20. 06	20. 70
750	17. 43	18. 01	18. 60	19. 22	19. 84	20. 49	21. 15	21. 82
800	18. 29	18. 90	19. 52	20. 17	20. 82	21. 50	22. 19	22. 90
850	19. 10	19. 74	20. 39	21. 06	21. 75	22. 45	23. 18	23. 92
900	19. 87	20. 53	21. 21	21. 91	22. 62	23. 35	24. 11	24. 88
950	20. 60	21. 29	21. 99	22. 72	23. 46	24. 22	25. 00	25. 80
1,000	21. 29	22. 00	22. 73	23. 47	24. 24	25. 03	25. 83	26. 66
1,050	21. 95	22. 68	23. 43	24. 20	24. 99	25. 80	26. 63	27. 48
1,100	22. 58	23. 33	24. 10	24. 89	25. 70	26. 54	27. 39	28. 27
1,150	23. 17	23. 94	24. 73	25. 54	26. 38	27. 23	28. 11	29. 01
1,200	23. 75	24. 54	25. 35	26. 18	27. 04	27. 91	28. 81	29. 74
1,250	24. 28	25. 09	25. 92	26. 77	27. 64	28. 54	29. 46	30. 40
1,300	24. 80	25. 63	26. 48	27. 35	28. 24	29. 15	30. 09	31. 06
1,350	25. 30	26. 14	27. 00	27. 89	28. 80	29. 73	30. 69	31. 67
1,400	25. 77	26. 63	27. 51	28. 41	29. 34	30. 29	31. 27	32. 27
1,450	26. 22	27. 09	27. 98	28. 91	29. 85	30. 81	31. 81	32. 82
1,500	26. 65	27. 54	28. 45	29. 39	30. 34	31. 33	32. 34	33. 37
1,550	27. 07	27. 97	28. 89	29. 84	30. 82	31. 82	32. 84	33. 89
1,600	27. 47	28. 39	29. 33	30. 29	31. 28	32. 29	33. 34	34. 40

TABLE 145.—*Elevation of the boiling point* [a] *of sucrose solutions above that of water at various vapor pressures*—Continued

Solids per 100 g. of water	Brix	Vapor pressure, pounds per square inch						
		2.8886	3.6269	4.5193	5.5908	6.8688	8.3837	10.168
		Vapor pressure, millimeters of mercury						
		149.38	187.56	233.71	289.13	355.22	433.56	525.84
		Boiling point of water, degrees centigrade						
		60	65	70	75	80	85	90
		Elevation, degrees centigrade, above the boiling point of water						
80 PERCENT PURITY [b]								
50	33. 33	0. 77	0. 80	0. 83	0. 85	0. 88	0. 91	0. 95
100	50. 00	1. 85	1. 92	1. 99	2. 06	2. 13	2. 20	2. 28
150	60. 00	3. 02	3. 13	3. 24	3. 35	3. 47	3. 59	3. 71
200	66. 67	4. 23	4. 38	4. 53	4. 69	4. 85	5. 02	5. 19
250	71. 43	5. 45	5. 64	5. 84	6. 04	6. 25	6. 47	6. 69
300	75. 00	6. 64	6. 88	7. 12	7. 37	7. 63	7. 89	8. 16
350	77. 78	7. 81	8. 09	8. 38	8. 67	8. 97	9. 27	9. 59
400	80. 00	8. 95	9. 27	9. 59	9. 93	10. 27	10. 62	10. 98
450	81. 82	10. 03	10. 39	10. 76	11. 13	11. 51	11. 91	12. 31
500	83. 33	11. 06	11. 46	11. 86	12. 27	12. 70	13. 13	13. 58
550	84. 62	12. 04	12. 48	12. 91	13. 36	13. 83	14. 30	14. 78
600	85. 71	12. 98	13. 44	13. 91	14. 40	14. 90	15. 40	15. 93
650	86. 67	13. 85	14. 35	14. 85	15. 37	15. 90	16. 45	17. 00
700	87. 50	14. 69	15. 22	15. 75	16. 30	16. 87	17. 44	18. 03
750	88. 24	15. 48	16. 04	16. 60	17. 18	17. 78	18. 38	19. 01
800	88. 89	16. 23	16. 89	17. 49	18. 10	18. 72	19. 36	20. 02
850	89. 47	16. 94	17. 55	18. 17	18. 80	19. 45	20. 11	20. 80
900	90. 00	17. 61	18. 24	18. 89	19. 54	20. 22	20. 91	21. 62
950	90. 48	18. 25	18. 90	19. 56	20. 25	20. 95	21. 66	22. 40
1,000	90. 91	18. 86	19. 53	20. 22	20. 92	21. 65	22. 39	23. 15
1,050	91. 30	19. 43	20. 12	20. 83	21. 56	22. 30	23. 07	23. 85
1,100	91. 67	19. 97	20. 68	21. 41	22. 16	22. 93	23. 71	24. 51
1,150	92. 00	20. 50	21. 23	21. 98	22. 74	23. 53	24. 33	25. 16
1,200	92. 31	20. 98	21. 74	22. 50	23. 28	24. 09	24. 91	25. 76
1,250	92. 59	21. 46	22. 23	23. 01	23. 81	24. 63	25. 47	26. 34
1,300	92. 86	21. 91	22. 69	23. 49	24. 31	25. 15	26. 01	26. 89
1,350	93. 10	22. 33	23. 13	23. 95	24. 78	25. 64	26. 52	27. 41
1,400	93. 33	22. 74	23. 55	24. 38	25. 23	26. 10	27. 00	27. 91
1,450	93. 55	23. 14	23. 96	24. 81	25. 67	26. 56	27. 47	28. 40
1,500	93. 75	23. 51	24. 35	25. 21	26. 09	26. 99	27. 91	28. 86
1,550	93. 94	23. 88	24. 73	25. 60	26. 49	27. 41	28. 35	29. 31
1,600	94. 12	24. 22	25. 09	25. 97	26. 87	27. 80	28. 75	29. 73

[a] See footnote *a*, p. 694–5.
[b] See footnote *b*, p. 696.

TABLE 145.—*Elevation of the boiling point* [a] *of sucrose solutions above that of water at various vapor pressures*—Continued

Solids per 100 g. of water	Vapor pressure, pounds per square inch							
	12.260	14.696	17.520	20.779	24.519	28.795	33.661	39.177
	Vapor pressure, millimeters mercury							
	634.02	760.00	906.04	1074.58	1267.99	1489.12	1740.77	2026.03
	Boiling point of water, degrees centigrade							
	95	100	105	110	115	120	125	130
	Elevation, degrees centigrade, above the boiling point of water							
	80 PERCENT PURITY [b]							
50	0. 98	1. 01	1. 04	1. 08	1. 11	1. 15	1. 19	1. 22
100	2. 35	2. 43	2. 51	2. 59	2. 68	2. 76	2. 85	2. 94
150	3. 83	3. 96	4. 09	4. 23	4. 36	4. 50	4. 65	4. 80
200	5. 36	5. 54	5. 72	5. 91	6. 10	6. 30	6. 50	6. 71
250	6. 91	7. 14	7. 38	7. 62	7. 87	8. 12	8. 38	8. 65
300	8. 43	8. 71	9. 00	9. 29	9. 60	9. 91	10. 23	10. 55
350	9. 91	10. 24	10. 58	10. 93	11. 28	11. 65	12. 02	12. 41
400	11. 35	11. 73	12. 12	12. 52	12. 92	13. 34	13. 77	14. 21
450	12. 73	13. 15	13. 58	14. 03	14. 49	14. 96	15. 44	15. 93
500	14. 03	14. 50	14. 98	15. 47	15. 98	16. 49	17. 03	17. 57
550	15. 28	15. 79	16. 31	16. 85	17. 40	17. 96	18. 54	19. 13
600	16. 46	17. 01	17. 57	18. 15	18. 74	19. 35	19. 97	20. 61
650	17. 57	18. 16	18. 76	19. 38	20. 01	20. 66	21. 32	22. 00
700	18. 64	19. 26	19. 90	20. 55	21. 22	21. 91	22. 62	23. 34
750	19. 65	20. 30	20. 97	21. 66	22. 37	23. 09	23. 84	24. 60
800	20. 69	21. 38	22. 09	22. 81	23. 56	24. 32	25. 10	25. 91
850	21. 49	22. 21	22. 94	23. 70	24. 47	25. 26	26. 08	26. 91
900	22. 35	23. 09	23. 85	24. 64	25. 44	26. 26	27. 11	27. 98
950	23. 15	23. 92	24. 71	25. 52	26. 36	27. 21	28. 09	28. 98
1,000	23. 92	24. 72	25. 54	26. 38	27. 24	28. 12	29. 03	29. 95
1,050	24. 65	25. 47	26. 31	27. 18	28. 06	28. 97	29. 91	30. 86
1,100	25. 34	26. 18	27. 04	27. 93	28. 85	29. 78	30. 74	31. 72
1,150	26. 00	26. 87	27. 76	28. 67	29. 61	30. 56	31. 55	32. 56
1,200	26. 62	27. 51	28. 42	29. 35	30. 31	31. 29	32. 30	33. 33
1,250	27. 22	28. 13	29. 06	30. 01	30. 99	32. 00	33. 03	34. 09
1,300	27. 80	28. 72	29. 67	30. 64	31. 64	32. 67	33. 72	34. 80
1,350	28. 34	29. 28	30. 25	31. 24	32. 26	33. 31	34. 38	35. 48
1,400	28. 85	29. 81	30. 79	31. 81	32. 84	33. 91	35. 00	36. 12
1,450	29. 35	30. 33	31. 33	32. 36	33. 42	34. 50	35. 61	36. 75
1,500	29. 83	30. 82	31. 84	32. 88	33. 96	35. 06	36. 19	37. 34
1,550	30. 29	31. 30	32. 33	33. 40	34. 48	35. 60	36. 75	37. 93
1,600	30. 73	31. 75	32. 80	33. 88	34. 98	36. 12	37. 28	38. 47

TABLE 145.—*Elevation of the boiling point* [a] *of sucrose solutions above that of water at various vapor pressures*—CONTINUED

Solids per 100 g. of water	Brix	Vapor pressure, pounds per square inch						
		2.8886	3.6269	4.5193	5.5908	6.8688	8.3837	10.168
		Vapor pressure, millimeters of mercury						
		149.38	187.56	233.71	289.13	355.22	433.56	525.84
		Boiling point of water, degrees centigrade						
		60	65	70	75	80	85	90
		Elevation, degrees centigrade, above the boiling point of water						
70 PERCENT PURITY [b]								
50	33.33	0.92	0.96	0.99	1.02	1.06	1.10	1.13
100	50.00	2.20	2.28	2.36	2.45	2.53	2.62	2.71
150	60.00	3.54	3.67	3.80	3.93	4.06	4.20	4.34
200	66.67	4.90	5.07	5.25	5.43	5.62	5.81	6.01
250	71.43	6.25	6.47	6.70	6.93	7.17	7.42	7.67
300	75.00	7.58	7.85	8.13	8.41	8.70	9.00	9.31
350	77.78	8.89	9.20	9.53	9.86	10.20	10.55	10.91
400	80.00	10.15	10.51	10.88	11.26	11.65	12.04	12.45
450	81.82	11.35	11.76	12.17	12.59	13.03	13.48	13.93
500	83.33	12.50	12.95	13.41	13.87	14.35	14.84	15.35
550	84.62	13.61	14.10	14.59	15.10	15.62	16.16	16.70
600	85.71	14.65	15.17	15.70	16.25	16.81	17.39	17.98
650	86.67	15.63	16.19	16.76	17.34	17.94	18.56	19.18
700	87.50	16.57	17.16	17.76	18.38	19.02	19.67	20.34
750	88.24	17.45	18.08	18.71	19.37	20.04	20.72	21.42
800	88.89	18.30	18.95	19.62	20.31	21.01	21.73	22.46
850	89.47	19.09	19.78	20.47	21.19	21.92	22.67	23.44
900	90.00	19.86	20.57	21.29	22.03	22.79	23.57	24.37
950	90.48	20.57	21.31	22.06	22.83	23.62	24.42	25.25
1,000	90.91	21.25	22.01	22.79	23.58	24.40	25.23	26.09
1,050	91.30	21.90	22.68	23.48	24.30	25.14	26.00	26.88
1,100	91.67	22.52	23.32	24.14	24.99	25.85	26.73	27.64
1,150	92.00	23.10	23.92	24.77	25.63	26.52	27.42	28.35
1,200	92.31	23.66	24.51	25.37	26.26	27.16	28.09	29.04
1,250	92.59	24.20	25.06	25.94	26.85	27.78	28.73	29.70
1,300	92.86	24.70	25.58	26.48	27.41	28.36	29.32	30.32
1,350	93.10	25.20	26.10	27.02	27.96	28.92	29.91	30.93
1,400	93.33	25.65	26.57	27.51	28.46	29.45	30.46	31.49
1,450	93.55	26.10	27.03	27.98	28.96	29.96	30.98	32.03
1,500	93.75	26.52	27.47	28.44	29.43	30.45	31.49	32.56
1,550	93.94	26.93	27.90	28.88	29.89	30.92	31.98	33.06
1,600	94.12	27.33	28.31	29.31	30.33	31.38	32.45	33.55

[a] See footnote *a*, p. 694-5.
[b] See footnote *b*, p. 696.

TABLE 145.—*Elevation of the boiling point* [a] *of sucrose solutions above that of water at various vapor pressures*—Continued

Solids per 100 g. of water	Vapor pressure, pounds per square inch							
	12.260	14.696	17.520	20.779	24.519	28.795	33.661	39.177
	Vapor pressure, millimeters of mercury							
	634.02	760.00	906.04	1074.58	1267.99	1489.12	1740.77	2026.03
	Boiling point of water, degrees centigrade							
	95	100	105	110	115	120	125	130
	Elevation, degrees centigrade, above the boiling point of water							
	70 PERCENT PURITY [b]							
50	1. 17	1. 21	1. 25	1. 29	1. 33	1. 38	1. 42	1. 47
100	2. 80	2. 89	2. 99	3. 08	3. 18	3. 29	3. 39	3. 50
150	4. 49	4. 64	4. 79	4. 95	5. 11	5. 28	5. 45	5. 62
200	6. 21	6. 42	6. 63	6. 85	7. 07	7. 30	7. 54	7. 78
250	7. 93	8. 19	8. 46	8. 74	9. 02	9. 32	9. 62	9. 92
300	9. 62	9. 94	10. 27	10. 61	10. 95	11. 31	11. 67	12. 04
350	11. 28	11. 65	12. 03	12. 43	12. 84	13. 25	13. 68	14. 12
400	12. 87	13. 30	13. 74	14. 19	14. 65	15. 13	15. 62	16. 12
450	14. 40	14. 88	15. 37	15. 88	16. 39	------	------	------
500	15. 86	16. 39	16. 93	17. 49	18. 06	------	------	------
550	17. 27	17. 84	18. 43	19. 04	19. 66	------	------	------
600	18. 58	19. 20	19. 83	20. 49	21. 15	------	------	------
650	19. 83	20. 49	21. 17	21. 86	22. 58	------	------	------
700	21. 02	21. 72	22. 44	23. 18	23. 93	------	------	------
750	22. 14	22. 88	23. 64	24. 41	25. 21	------	------	------
800	23. 22	23. 99	24. 78	25. 60	26. 43	------	------	------
850	24. 23	25. 03	25. 86	26. 71	27. 58	------	------	------
900	25. 19	26. 03	26. 89	27. 77	28. 68	------	------	------
950	26. 10	26. 97	27. 86	28. 78	29. 72	------	------	------
1,000	26. 96	27. 86	28. 78	29. 73	30. 70	------	------	------
1,050	27. 79	28. 71	29. 66	30. 63	31. 63	------	------	------
1,100	28. 57	29. 52	30. 49	31. 50	32. 53	------	------	------
1,150	29. 31	30. 28	31. 28	32. 31	33. 36	------	------	------
1,200	30. 02	31. 02	32. 04	33. 10	34. 18	------	------	------
1,250	30. 70	31. 72	32. 77	33. 85	34. 95	------	------	------
1,300	31. 34	32. 38	33. 45	34. 55	35. 68	------	------	------
1,350	31. 97	33. 03	34. 12	35. 24	36. 39	------	------	------
1,400	32. 55	33. 63	34. 74	35. 88	37. 05	------	------	------
1,450	33. 11	34. 21	35. 34	36. 50	37. 69	------	------	------
1,500	33. 65	34. 77	35. 92	37. 10	38. 31	------	------	------
1,550	34. 17	35. 31	36. 48	37. 68	38. 90	------	------	------
1,600	34. 68	35. 83	37. 01	38. 23	39. 48	------	------	------

323414°—42——46

TABLE 146.—*Purity factors for use with dry-lead defecation* [1]

[The direct polariscope reading of the solution times the factor corresponding to the Brix gives the coefficient of purity]

Brix	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	----------	260.6336	130.2660	86.8102	65.0829	52.0461	43.3549	37.1469	32.4909	28.8695
1	25.9725	23.6022	21.6269	19.9556	18.5230	17.2814	16.1951	15.2365	14.3845	13.6221
2	12.9360	12.3152	11.7508	11.2355	10.7632	10.3286	9.9275	9.5561	9.2113	8.8901
3	8.5905	8.3102	8.0473	7.8004	7.5680	7.3490	7.1420	6.9463	6.7608	6.5849
4	6.4178	6.2588	6.1074	5.9630	5.8253	5.6936	5.5676	5.4470	5.3314	5.2206
5	5.1142	5.0120	4.9136	4.8191	4.7280	4.6402	4.5555	4.4738	4.3950	4.3188
6	4.2451	4.1739	4.1050	4.0382	3.9755	3.9109	3.8501	3.7912	3.7330	3.6784
7	3.6244	3.5720	3.5209	3.4713	3.4231	3.3761	3.3304	3.2858	3.2424	3.2001
8	3.1589	3.1186	3.0794	3.0411	3.0037	2.9671	2.9315	2.8966	2.8626	2.8293
9	2.7968	2.7649	2.7338	2.7033	2.6735	2.6443	2.6157	2.5877	2.5603	2.5334
10	2.5071	2.4813	2.4560	2.4312	2.4068	2.3830	2.3596	2.3366	2.3140	2.2919
11	2.2701	2.2488	2.2278	2.2072	2.1870	2.1671	2.1475	2.1283	2.1095	2.0909
12	2.0727	2.0547	2.0370	2.0197	2.0026	1.9858	1.9692	1.9529	1.9369	1.9211
13	1.9056	1.8903	1.8752	1.8603	1.8457	1.8313	1.8171	1.8031	1.7893	1.7757
14	1.7623	1.7491	1.7361	1.7233	1.7106	1.6981	1.6858	1.6737	1.6617	1.6499
15	1.6382	1.6267	1.6154	1.6042	1.5931	1.5822	1.5714	1.5608	1.5503	1.5399
16	1.5296	1.5195	1.5095	1.4997	1.4899	1.4803	1.4708	1.4614	1.4521	1.4429
17	1.4338	1.4249	1.4160	1.4072	1.3986	1.3900	1.3816	1.3732	1.3649	1.3567
18	1.3487	1.3407	1.3328	1.3249	1.3172	1.3095	1.3020	1.2945	1.2871	1.2797
19	1.2725	1.2653	1.2582	1.2511	1.2442	1.2373	1.2305	1.2237	1.2171	1.2104
20	1.2039	1.1974	1.1910	1.1846	1.1784	1.1721	1.1660	1.1598	1.1538	1.1478
21	1.1419	1.1360	1.1302	1.1244	1.1187	1.1130	1.1074	1.1018	1.0963	1.0909
22	1.0855	1.0801	1.0748	1.0696	1.0643	1.0592	1.0540	1.0490	1.0439	1.0389
23	1.0340	1.0291	1.0242	1.0194	1.0146	1.0099	1.0052	1.0005	0.9959	0.9913
24	0.9868	0.9823	0.9778	0.9734	0.9690	0.9647	0.9603	0.9560	.9518	.9476
25	.9434	----------	----------	----------	----------	----------	----------	----------	----------	----------

[1] E. W. Rice, Facts About Sugar **22**, 1066 (1927).

TABLE 147.—*International atomic weights, 1941*

[Partial list]

Element	Symbol	Atomic No.	Atomic weight	Element	Symbol	Atomic No.	Atomic weight
Aluminum	Al	13	26. 97	Magnesium	Mg	12	24. 32
Antimony	Sb	51	121. 76	Manganese	Mn	25	54. 93
Arsenic	As	33	74. 91	Mercury	Hg	80	200. 61
Barium	Ba	56	137. 36	Molybdenum	Mo	42	95. 95
Bismuth	Bi	83	209. 00	Neon	Ne	10	20. 183
Boron	B	5	10. 82	Nickel	Ni	28	58. 69
Bromine	Br	35	79. 916	Nitrogen	N	7	14. 008
Cadmium	Cd	48	112. 41	Oxygen	O	8	16. 0000
Calcium	Ca	20	40. 08	Phosphorus	P	15	30. 98
Carbon	C	6	12. 010	Platinum	Pt	78	195. 23
Chlorine	Cl	17	35. 457	Potassium	K	19	39. 096
Chromium	Cr	24	52. 01	Radium	Ra	88	226. 05
Cobalt	Co	27	58. 94	Selenium	Se	34	78. 96
Copper	Cu	29	63. 57	Silicon	Si	14	28. 06
Fluorine	F	9	19. 00	Silver	Ag	47	107. 880
Gallium	Ga	31	69. 72	Sodium	Na	11	22. 997
Gold	Au	79	197. 2	Strontium	Sr	38	87. 63
Helium	He	2	4. 003	Sulfur	S	16	32. 06
Hydrogen	H	1	1. 0080	Tin	Sn	50	118. 70
Iodine	I	53	126. 92	Tungsten	W	74	183. 92
Iridium	Ir	77	193. 1	Uranium	U	92	238. 07
Iron	Fe	26	55. 85	Vanadium	V	23	50. 95
Lead	Pb	82	207. 21	Zinc	Zn	30	65. 38
Lithium	Li	3	6. 940				

TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*

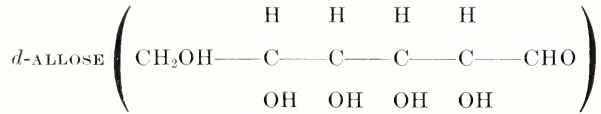
[This table lists the melting points, optical rotations, and molecular weights of a selected group of sugars and derivatives.

Unfortunately, there is no universally accepted nomenclature for the sugar derivatives, and therefore names have been selected to conform as far as possible with the general principles of established nomenclature for organic compounds. The alpha and beta modifications of the heptoses and higher sugars have been named according to the suggestion of Isbell, while the alpha and beta names in common use have been retained for the lower sugars.

With only a few exceptions (where the importance of the compound makes inclusion desirable) only crystalline compounds are given. The derivatives are listed under the parent sugar in the following order: hydrazones, osazones, methyl ethers, acetates, halogeno-acetates, glycosides, acetone derivatives, acids, lactones, amides, hydrazides, and glycals. A comprehensive list of well-defined crystalline derivatives of sucrose and glucose is included.

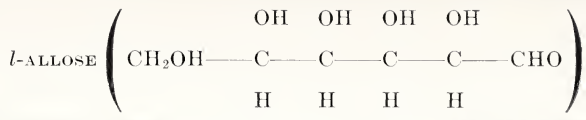
For the calculation of the molecular weights, the 1938 International Atomic Weights were used. The specific rotations are given for the *D* line of sodium and for a temperature of 20° C except where a different wave length is given or a different temperature is noted in parentheses. The literature to January 1, 1938, has been covered, and the more important compounds have been included.]

d-ALLOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[*M*]	Concentration	Solvent[1]
				°*C*			*g/100 ml*	
β-*d*-Allose	[1]	$C_6H_{12}O_6$	180. 16	128–128. 5	[2]−0. 2→+14. 4	−40	5	H_2O
d-Allonic γ-lactone	[2]	$C_6H_{10}O_6$	178. 14	97–120	−6. 8	−1, 210	11	H_2O
d-Allonic phenylhydrazide	[3]	$C_{12}H_{18}O_5N_2$	286. 28	----------	+25. 9	+7, 410	1	H_2O

l-ALLOSE



β-*l*-Allose	[4]	$C_6H_{12}O_6$	180. 16	128–129	−1. 90→−13. 9	−350	4	H_2O
l-Allose *p*-bromphenylhydrazone	[4]	$C_{12}H_{17}O_5N_2Br$	349. 19	141–145	+6. 4	+2, 300		EtOH
l-Allonic γ-lactone	[4]	$C_6H_{10}O_6$	178. 14	130	+6. 3 (25°)	+1, 100		H_2O
l-Allonic phenylhydrazide	[5]	$C_{12}H_{18}O_6N_2$	286. 28	142–145	−23. 6	−6, 760		H_2O

[1] These values are read at 20° C, except where the temperature is specified otherwise in parentheses.
[2] Values from reference [1] extrapolated to zero time.

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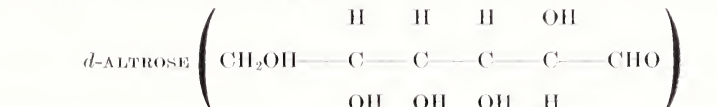
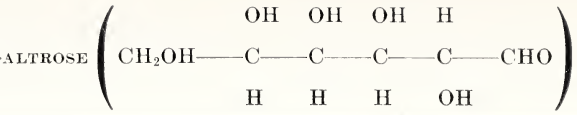
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-ALTROSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
β-*d*-Altrose	[1]	$C_6H_{12}O_6$	180. 16	103–105	+32. 6[2]		8	H_2O
d-Altrose dibenzylmercaptal	[1]	$C_{20}H_{26}O_5S_2$	410. 53	121–122	+39. 4	+16, 200	3	Pyridine
Diacetone-*d*-altrose	[2]	$C_{12}H_{20}O_6$	260. 28	89	+28. 27	+7, 400	2	Acetone
Methyl tetramethyl-α-*d*-altroside	[4]	$C_{11}H_{22}O_6$	250. 29	76–78	+97.4	+24, 400	1	EtOH
Methyl 2-methyl-α-*d*-altroside	[5]	$C_8H_{16}O_6$	208. 21	81–83	+111.6 (15°)	+23, 200	1	$CHCl_3$

l-ALTROSE



β-*l*-Altrose	[3]	$C_6H_{12}O_6$	180. 16	107–109. 5	−28.8→−32.3	−5, 180	4	H_2O
l-Altrose benzylphenylhydrazone	[3]	$C_{19}H_{24}O_5N_2$	360. 40	147–148				
l-Altronic acid	[6]	$C_6H_{12}O_7$	196. 16	110	−8.1	−1, 600		H_2O
l-Altronic phenylhydrazide	[6]	$C_{12}H_{18}O_6N_2$	286. 28	151–152	+18.4	+5, 300		H_2O

[1] These values are read at 20° C, except where the temperature is specified otherwise in parentheses.
[2] Equilibrium rotation; no mutarotation recorded.

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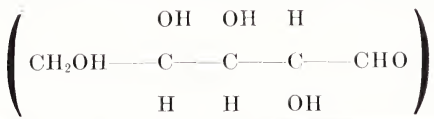
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

l-ARABINOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
β-*l*-Arabinose	[1, 2, 3]	$C_5H_{10}O_5$	150. 13	160	+190.6→+104.5	+28, 610	--------	H_2O
α-*l*-Arabinose.$CaCl_2$.$4H_2O$	[1, 3, 4]	$C_5H_{18}O_9CaCl_2$	333. 19	204	+34.7→+48.0	+11, 560	9	H_2O
l-Arabinose benzylphenylhydrazone	[5, 6]	$C_{18}H_{22}O_4N_2$	330. 38	174	−14.8→−11.5	−4, 890	--------	MeOH
2,3,4-Trimethyl-α-*l*-arabinose	[7, 8]	$C_8H_{16}O_5$	192. 21	[2] 81–82	+16. 4	+3, 150	5	$CHCl_3$
1,1′,2,3,4,5-Hexaacetyl-*l*-arabinose	[9]	$C_{17}H_{24}O_{12}$	420. 36	89. 5	−27 (27°)	−11, 300	4	$CHCl_3$
1,2,3,4-Tetraacetyl-α-*l*-arabinose	[10]	$C_{13}H_{18}O_9$	318. 28	97	+42.5 (22°)	+13. 500	3	$CHCl_3$
1,2,3,4-Tetraacetyl-β-*l*-arabinose	[10]	$C_{13}H_{18}O_9$	318. 28	86	+147.2 (21°)	+46, 800	5	$CHCl_3$
2,3,4,5-Tetraacetyl-*l*-arabinose	[11]	$C_{13}H_{18}O_9$	318. 28	113–115	−65.6 (27°)	−20, 880	4	$CHCl_3$
1-Chloro-1,2,3,4,5-pentaacetyl-*l*-arabinose.	[12]	$C_{15}H_{21}O_{10}Cl$	396. 78	109–110	−96 (25°)	−38, 100	4	$CHCl_3$
1-Bromo-1,2,3,4,5-pentaacetyl-*l*-arabinose.	[12]	$C_{15}H_{21}O_{10}Br$	441. 24	130–131	−134 (23°)	−59, 100	4	$CHCl_3$
1-Fluoro-2,3,4-triacetyl-β-*l*-arabinose	[13]	$C_{11}H_{15}O_7F$	278. 23	117–118	+138.2	+38, 500	2	$CHCl_3$
1-Chloro-2,3,4-triacetyl-β-*l*-arabinose	[13]	$C_{11}H_{15}O_7Cl$	294. 69	146–147	+244. 4	+72, 000	2	$CHCl_3$
1-Bromo-2,3,4-triacetyl-β-*l*-arabinose	[13]	$C_{11}H_{15}O_7Br$	339. 15	138–139	+287.1	+97, 400	2	$CHCl_3$
1-Iodo-2,3,4-triacetyl-β-*l*-arabinose	[13]	$C_{11}H_{15}O_7I$	386. 15	d	+339.1	+130, 900	2	$CHCl_3$
Methyl α-*l*-arabinopyranoside	[14]	$C_6H_{12}O_5$	164. 16	131	+17.3	+2, 840	3	H_2O
Methyl β-*l*-arabinopyranoside	[14]	$C_6H_{12}O_5$	164. 16	169	+245.5	+40, 300	7	H_2O
Methyl triacetyl-β-*l*-arabinopyranoside.	[10]	$C_{12}H_{18}O_8$	290. 27	85	+182.0 (23°)	+52, 800	4	$CHCl_3$
Methyl trimethyl-α-*l*-arabinopyranoside.	[8, 15]	$C_9H_{18}O_5$	206. 24	46–48	+46.2	+9, 530	1	H_2O
Methyl trimethyl-β-*l*-arabinopyranoside.	[15]	$C_9H_{18}O_5$	206. 24	44–46	+250	+51, 600	1	H_2O

l-Arabonic acid	[16, 17]	$C_5H_{10}O_6$	166. 13	111–116	−9.8	−1, 630	5	H_2O
l-Arabonic γ-lactone	[16, 19]	$C_5H_8O_5$	148. 11	95–98	−71.6	−10, 600	5	H_2O
l-Arabonic phenylhydrazide	[20]	$C_{11}H_{16}O_5N_2$	256. 26	215				
l-Arabonic amide	[21]	$C_5H_{11}O_5N$	165. 15	136	+37.5	+6, 190	5	H_2O
l-Arabinal	[22, 23, 24]	$C_5H_8O_3$	116. 11	81–83	−202.8 (19°)	−23, 550	3	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Possibly contaminated by the beta isomer.

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

CELLOBIOSE (4-(β-*d*-glucopyranosido)-*d*-glucose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
β-Cellobiose	[1, 2]	$C_{12}H_{22}O_{11}$	342. 30	225	+14.2→+34.6	+4, 860	8	H_2O
Cellobiose phenylosazone	[4, 5]	$C_{24}H_{32}O_9N_4$	520. 53	198–200	−6.5 (18°)	−3, 400	1	Pyridine+EtOH (2:3)
Heptamethyl-α-cellobiose	[6]	$C_{19}H_{36}O_{11}$	440. 48	105–110	+53→+40$[\alpha]_{578}$	+23, 000	1	H_2O
Octaacetyl-*aldehydo*-cellobiose	[7]	$C_{28}H_{38}O_{19}$	678. 59	Sirup	+17.7	--------	3	$CHCl_3$
Octaacetyl-α-cellobiose	[3, 8]	$C_{28}H_{38}O_{19}$	678. 59	229	+41.0	+27, 800	6	$CHCl_3$
Octaacetyl-β-cellobiose	[8]	$C_{28}H_{38}O_{19}$	678. 59	202	−14.7	−10, 000	5	$CHCl_3$
1-Fluoro-heptaacetyl-α-cellobiose	[9]	$C_{26}H_{35}O_{17}F$	638. 54	187	+30.6	+19, 500	2	$CHCl_3$
1-Chloro-heptaacetyl-α-cellobiose	[9, 10]	$C_{26}H_{35}O_{17}Cl$	655. 00	200–201	+71.7	+47, 000	2	$CHCl_3$
1-Bromo-heptaacetyl-α-cellobiose	[9, 11]	$C_{26}H_{35}O_{17}Br$	699. 46	180 d.	+95.8	+67, 000	2	$CHCl_3$
1-Iodo-heptaacetyl-α-cellobiose	[9, 11]	$C_{26}H_{35}O_{17}I$	746. 46	160–170	+125.7	+93, 800	2	$CHCl_3$
Methyl α-cellobioside	[12]	$C_{13}H_{24}O_{11}$	356. 32	144–145	+96.8	+34, 490	1	H_2O
Methyl β-cellobioside	[13]	$C_{13}H_{24}O_{11}$	356. 32	193	−19.1 (17°)	− 6, 810	9	H_2O
Methyl heptaacetyl-α-cellobioside	[12]	$C_{27}H_{38}O_{18}$	650. 58	185	+55.7	+36, 200	1	$CHCl_3$
Methyl heptaacetyl-β-cellobioside	[14]	$C_{27}H_{38}O_{18}$	650. 58	187	−25.7	−16, 720	6	$CHCl_3$
Methyl heptamethyl-β-cellobioside	[15,16,17]	$C_{20}H_{38}O_{11}$	454. 51	86	−15.9	−7, 230	1	H_2O
Cellobial	[18, 19]	$C_{12}H_{20}O_9$	308. 28	175–176	+1.0	+ 300	9	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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CELTROBIOSE (4-(β-*d*-GLUCOPYRANOSIDO)-*d*-ALTROSE)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$	$[M]$	Concentration	Solvent
				°*C*			*g/100 ml*	
Celtrobiose.H_2O	[1]	$C_{12}H_{24}O_{12}$	360. 31	133–148	+13.6	+ 4, 900	5	H_2O
Heptaacetyl-α-celtrobiose	[1]	$C_{26}H_{36}O_{18}$	636. 55	130–131	+22.3→+15.1	+14, 200	5	$CHCl_3$
Heptaacetyl-β-celtrobiose [2]	[1]	$C_{26}H_{36}O_{18}$	636. 55	----------	+3.9→+15.1	+ 2, 500	10	$CHCl_3$
Octaacetyl-α-celtrobiose	[1]	$C_{28}H_{38}O_{19}$	678. 59	129–130 112	+48.0	+32, 600	4	$CHCl_3$
Octaacetyl-β-celtrobiose	[1]	$C_{28}H_{38}O_{19}$	678. 59	103–105 113–114	−13.0	− 8, 800	6	$CHCl_3$
Heptaacetylceltrobiose	[1]	$C_{26}H_{36}O_{18}$	636. 55	216	+1.0	+ 600	1	$CHCl_3$
1-Chloro-heptaacetyl-α-celtrobiose	[1, 2]	$C_{26}H_{35}O_{17}Cl$	655. 00	141–142	+64.2	+42, 000	4	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Separates as monoetherate. Rotation calculated on solvent-free basis.

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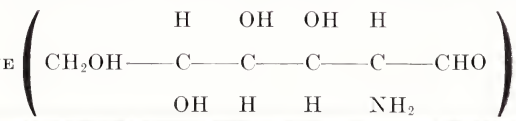
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

CHONDROSAMINE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
Pentaacetyl-α-*d*-chondrosamine	[1, 2]	$C_{16}H_{23}O_{10}N$	389. 35	183	+101.3(18°)	+39, 400	2	$CHCl_3$
Pentaacetyl-β-*d*-chondrosamine	[1, 2]	$C_{16}H_{23}O_{10}N$	389. 35	235 d.	+ 11.0	+ 4, 300	1	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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DESOXY SUGARS

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
2-Desoxycellobiose	[1, 2]	$C_{12}H_{22}O_{10}$	326. 30	184–200	+23.2 (21°)	+ 7, 570	8	H_2O
β-*d*-2-Desoxyglucose	[3, 4]	$C_6H_{12}O_5$	164. 16	148	+15.0→+90.2 [2]	--------	2	Pyridine
β-*d*-2-Desoxygalactose	[5]	$C_6H_{12}O_5$	164. 16	121	+40.8→+60.5 [3]	+ 6, 700	4	H_2O
β-*d*-2-Desoxyxylose	[6]	$C_5H_{10}O_4$	134. 13	92–96	−22.5 [4]→−2.0(22°)	--------	2	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Rotations at 5 minutes and 24 hours.
[3] Complex mutarotation.
[4] Rotation after several minutes.

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DIFRUCTOSE ANHYDRIDES

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
Difructose anhydride I	[1, 2, 3, 4]	$C_{12}H_{20}O_{10}$	324. 28	164	+27.0	+8, 760	4	H_2O
Hexaacetyldifructose anhydride I	[1, 4]	$C_{24}H_{32}O_{16}$	576. 50	137	+0.54	+311	10	$CHCl_3$
Hexamethyldifructose anhydride I	[5, 6]	$C_{18}H_{32}O_{10}$	408. 44	Sirup	+23.7	--------	5	$CHCl_3$
					+50.4	--------	2	H_2O
3,4,3′,4′-tetraacetyldifructose anhydride I	[6]	$C_{20}H_{28}O_{14}$	492. 43	173	+23.0	+11, 320	3	H_2O
					−9.9	−4, 870	4	$CHCl_3$
3,4,3′,4′-Tetraacetyl-6,6′-dimethyldifructose anhydride I.	[6]	$C_{22}H_{32}O_{14}$	520. 48	128	+10.8	+5, 620	1	$CHCl_3$
3,4,3′,4′,-Tetraacetyl-6,6′-ditrityldifructose anhydride I.	[6]	$C_{58}H_{56}O_{14}$	977. 03	194	+21.1	+20, 610	4	$CHCl_3$
6,6′-Ditrityldifructose anhydride I	[6]	$C_{50}H_{48}O_{10}$	808. 89	195	+20.4(22°)	+16, 500	2	$CHCl_3$
Difructose anhydride II	[7]	$C_{12}H_{20}O_{10}$	324. 28	198	+13.8	+4, 470	9	H_2O
Hexamethyldifructose anhydride II	[6]	$C_{18}H_{32}O_{10}$	408. 44	73	−28.2	−11, 520	4	$CHCl_3$
					+6.0	+2, 450	4	H_2O
Difructose anhydride III	[6, 7]	$C_{12}H_{20}O_{10}$	324. 28	162	+135.6	+43, 970	8	H_2O
Hexamethyldifructose anhydride III	[6]	$C_{18}H_{32}O_{10}$	408. 44	Sirup	+157.9	--------	4	$CHCl_3$
					+164.5	--------	2	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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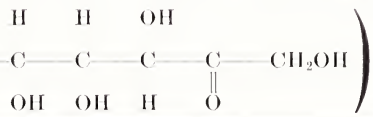
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-FRUCTOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$	$[M]$	Concentration	Solvent
				°C			g/100 ml	
β-*d*-Fructose	[1]	$C_6H_{12}O_6$	180.16	102–104	−132.2 → −92.4	−23,820	4	H_2O
3-Methyl-*d*-fructose	[2, 3]	$C_7H_{14}O_6$	194.18	128–130	−84.1[2] → −53.5		1	H_2O
					−74.1 → −22.1	−14,390	1	MeOH
3,4,6-Trimethyl-*d*-fructose	[4]	$C_9H_{18}O_6$	222.24	Sirup	+30.5 (15°)		1	H_2O
					+26.6 (15°)		1	$CHCl_3$
1,3,4-Trimethyl-*d*-fructose	[5]	$C_9H_{18}O_6$	222.24	73	−23.8 → −51.8	−11,500	8	H_2O
					+16.5	+3,670	1	$CHCl_3$
1,3,4,5-Tetramethyl-*d*-fructose	[6]	$C_{10}H_{20}O_6$	236.26	98–99	−99.0 → −95.6	−22,600	5	MeOH
					−124.7 → −121.3	−28,660	5	H_2O
1,3,4,6-Tetramethyl-*d*-fructose	[7]	$C_{10}H_{20}O_6$	236.26	Sirup	+31.3 (16°)		2	H_2O
					+21.3		2	MeOH
1,3,4,5-Tetraacetyl-*d*-fructose	[8]	$C_{14}H_{20}O_{10}$	348.30	131–132	−91.6	−31,900	3	$CHCl_3$
2,3,4,5-Tetraacetyl-*d*-fructose	[9]	$C_{14}H_{20}O_{10}$	348.30	112	+50.6	+17,600	3	$CHCl_3$
1,2,3,4,5-Pentaacetyl-α-*d*-fructose	[10]	$C_{16}H_{22}O_{11}$	390.34	122–123	+47.4	+18,500	3	$CHCl_3$
1,2,3,4,5-Pentaacetyl-β-*d*-fructose	[11]	$C_{16}H_{22}O_{11}$	390.34	108–109	−120.9	−47,200	5	$CHCl_3$
1,3,4,5,6-Pentaacetyl-*d*-fructose	[12]	$C_{16}H_{22}O_{11}$	390.34	70	+34.7	+13,500	8	$CHCl_3$
1,3,4,5-Tetrabenzoyl-*d*-fructose	[13]	$C_{34}H_{28}O_{10}$	596.57	174–175	−164.9	−98,400	4	$CHCl_3$
1,3,4,5, 6-Pentabenzoyl-*d*-fructose	[13]	$C_{41}H_{32}O_{11}$	700.67	124–125	+40.9	+28,700	3	$CHCl_3$
2-Fluoro-1,3,4,5-tetraacetyl-β-*d*-fructose.	[14]	$C_{14}H_{19}O_9F$	350.29	112	−90.4	−31,700	6	$CHCl_3$
2-Chloro-1,3,4,5-tetraacetyl-β-*d*-fructose.	[15]	$C_{14}H_{19}O_9Cl$	366.75	83	−160.9	−59,000	2	$CHCl_3$
2-Bromo-1,3,4,5-tetraacetyl-β-*d*-fructose.	[14]	$C_{14}H_{19}O_9Br$	411.21	65	−189.4	−77,800	3	$CHCl_3$

1,3,4,5-Tetraacetyl-6-chloro-*d*-fructose	[15]	$C_{14}H_{19}O_9Cl$	366.75	108	+45.3	+16, 600	2	$CHCl_3$
Methyl *α*-*d*-fructopyranoside	[16]	$C_7H_{14}O_6$	194.18	96–97	+44	+8, 500	1	H_2O
Methyl *β*-*d*-fructopyranoside	[17]	$C_7H_{14}O_6$	194.18	119–120	−172.1	−33, 400	10	H_2O
Methyl 1,3,4,5-tetraacetyl-*α*-*d*-fructopyranoside.	[16]	$C_{15}H_{22}O_{10}$	362.33	112	+45.0	+16, 300	1	$CHCl_3$
Methyl 1,3,4,5-tetraacetyl-*β*-*d*-fructopyranoside.	[17]	$C_{15}H_{22}O_{10}$	362.33	75–76	−124.6	−45, 100	8	$CHCl_3$
Methyl 1,3,4,5-tetrabenzoyl-*β*-*d*-fructopyranoside.	[13]	$C_{35}H_{30}O_{10}$	610.59	113	−171.3	−104, 600	5	$CHCl_3$
Methyl *d*-fructofuranoside	[18]	$C_7H_{14}O_6$	194.18	69	+93.1	+18, 100	2	H_2O
2,3-4,5-Diacetone-*d*-fructose	[2, 19, 20]	$C_{12}H_{20}O_6$	260.28	97	−32.9 (22°) −33.83 (22°)	−8, 560 −8, 800	3 4	H_2O Acetone.
1,2-4,5-Diacetone-*d*-fructose	[2,19,20, 21]	$C_{12}H_{20}O_6$	260.28	119–120	−161.3 −154 (23°) −146.6	−41, 980 −40, 100 −38, 160	7 4 2	H_2O Acetone. $CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Value after 15 minutes.

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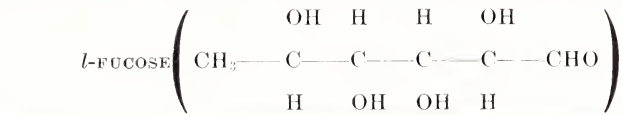
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

l-FUCOSE



Substance	Reference	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C				
α-*l*-Fucose	[1, 2, 3]	$C_6H_{12}O_5$	164. 16	145	−152. 6→−75. 9	−25, 100	4	H_2O
l-Fucose phenylhydrazone	[4, 5]	$C_{12}H_{18}O_4N_2$	254. 28	170–173				
1,2,3,4-Tetraacetyl-α-*l*-fucose	[6]	$C_{14}H_{20}O_9$	332. 30	92–93	−120 (34°)	−39, 800	2	$CHCl_3$
2,3,4,5-Tetraacetyl-*l*-fucose	[6]	$C_{14}H_{20}O_9$	332. 30	166–167	+40 (25°)	+13, 300	2	$(CHCl_2)_2$
Methyl α-*l*-fucopyranoside	[7]	$C_7H_{14}O_5$	178. 18	157. 5–158. 5	−197. 4	−35, 100	5	H_2O
Methyl β-*l*-fucopyranoside	[7]	$C_7H_{14}O_5$	178. 18	117–119	+16. 0	+2, 900	1	H_2O
Methyl 2,3,4-triacetyl-α-*l*-fucopyranoside	[8]	$C_{13}H_{20}O_8$	304. 29	74	−151	−45, 950	10	$CHCl_3$
Methyl 2,3,4-triacetyl-β-*l*-fucopyranoside	[8]	$C_{13}H_{20}O_8$	304. 29	99	+7. 0	+2, 100	10	$CHCl_3$
Monoacetone-*l*-fucose	[9]	$C_9H_{16}O_5$	204. 22	57	−62. 28	−12, 700		
Diacetone-*l*-fucose	[10]	$C_{12}H_{20}O_5$	244. 28	37	+52. 2 (18°)	+12, 750		None.
l-Fuconic γ-lactone	[12]	$C_6H_{10}O_5$	162. 14	106–107	+78. 3	+12, 700	3	H_2O
l-Fuconic amide	[11]	$C_6H_{13}O_5N$	179. 17	180	−31. 1	−5, 570	2	H_2O
l-Fuconic phenylhydrazide	[12]	$C_{12}H_{18}O_5N_2$	270. 28	203–204				

[1] These values are read at 20° C. except where the temperature is specified otherwise in parentheses.

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-GALACTOSE

```
                H     OH    OH    H
CH2OH——C——C——C——C——CHO
                OH    H     H     OH
```

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C.			g/100 ml	
α-*d*-Galactose	[1, 2, 3, 4, 5]	$C_6H_{12}O_6$	180. 16	167	+150.7→+80.2	+27, 150	5	H_2O
β-*d*-Galactose	[1, 2, 3, 4, 5]	$C_6H_{12}O_6$	180. 16	--------	+52.8→+80.2	+9, 510	4	H_2O
d-Galactose *o*-tolylhydrazone	[6, 7]	$C_{13}H_{20}O_5N_2$	284. 31	176	--------	--------	--------	
2-Methyl-β-*d*-galactose	[8]	$C_7H_{14}O_6$	194. 18	147–149	+53.0 [2]→+82.6	--------	5	H_2O
6-Methyl-α-*d*-galactose	[9]	$C_7H_{14}O_6$	194. 18	128	+114 [2]→+77$[\alpha]_{578}^{22}$	--------	8	H_2O
2,6-Dimethyl-β-*d*-galactose	[8]	$C_8H_{16}O_6$	208. 21	128–130	+46.8 [2]→+87.5	--------	6	H_2O
2,3,4-Trimethyl-α-*d*-galactose	[10, 11 12, 13]	$C_9H_{18}O_6$	222. 24	85	+154.1→+122 (21°)	+34, 250	2	H_2O
2,3,4,6-Tetramethyl-α-*d*-galactose	[14, 35]	$C_{10}H_{20}O_6$	236. 26	71	+150.5→+119.9(25°)	+35, 560	--------	--------
2,3,4,6-Tetraacetyl-α-*d*-galactose	[15, 26]	$C_{14}H_{20}O_{10}$	348. 30	133	+144.4→+90.7	+50, 300	1	$CHCl_3$
2,3,4,6-Tetraacetyl-β-*d*-galactose	[16, 18]	$C_{14}H_{20}O_{10}$	348. 30	112	+23.3	+8, 120	5	$CHCl_3$
2,3,5,6-Tetraacetyl-*d*-galactose	[17, 18]	$C_{14}H_{20}O_{10}$	348. 30	71–73	−17.8	−6, 200	5	$CHCl_3$
2,3,4,5,6-Pentaacetyl-*d*-galactose	[19]	$C_{16}H_{22}O_{11}$	390. 34	121	−25 (26°)	−9, 760	4	$CHCl_3$
1,2,3,5,6-Pentaacetyl-β-*d*-galactose [3]	[17]	$C_{16}H_{22}O_{11}$	390. 34	87	+61.2	+23, 890	4	$CHCl_3$
1,2,3,5,6-Pentaacetyl-α-*d*-galactose [3]	[20]	$C_{16}H_{22}O_{11}$	390. 34	98	−41.6	−16, 240	--------	$CHCl_3$
1,2,3,4,6-Pentaacetyl-α-*d*-galactose	[21, 22]	$C_{16}H_{22}O_{11}$	390. 34	96	+106.7	+41, 650	3	$CHCl_3$
1,2,3,4,6-Pentaacetyl-β-*d*-galactose	[17, 21, 22]	$C_{16}H_{22}O_{11}$	390. 34	142	+25	+9, 760	--------	$CHCl_3$
1,2,3,4,5-Pentaacetyl-α-*d*-galactose	[23]	$C_{16}H_{22}O_{11}$	390. 34	128	−11.0	−4, 300	1	$CHCl_3$
1,2,3,4,5-Pentaacetyl-β-*d*-galactose	[23]	$C_{16}H_{22}O_{11}$	390. 34	101	−78.3 (18°)	−30, 560	1	$CHCl_3$
1,1′,2,3,4,5,6-Heptaacetyl-*d*-galactose	[24]	$C_{20}H_{28}O_{14}$	492. 43	106	+4.0	+1, 970	--------	$CHCl_3$
1-Chloro-2,3,5,6-tetraacetyl-*d*-galactose	[17]	$C_{14}H_{19}O_9Cl$	366. 75	67	−77.1	−28, 280	6	$CHCl_3$

TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-GALACTOSE

```
                H     OH    OH    H
CH2OH——C——C——C——C——CHO
                OH    H     H     OH
```

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20.1}$	$[M]$	Concentration	Solvent
1-Chloro-2,3,4,6-tetraacetyl-α-*d*-galactose	[25]	$C_{14}H_{19}O_9Cl$	366.75	82–83	+212.2	+77,820	1	$CHCl_3$
1-Chloro-2,3,4,6-tetraacetyl-β-*d*-galactose	[26]	$C_{14}H_{19}O_9Cl$	366.75	93–94	+5.8 (22°)	+2,130	1	CCl_4
1-Bromo-2,3,4,6-tetraacetyl-α-*d*-galactose	[25, 27]	$C_{14}H_{19}O_9Br$	411.21	82–83	+236.4	+97,210	9	C_6H_6
1-Chloro-1′,2,3,4,5,6-hexacetyl-*d*-galactose	[28]	$C_{18}H_{25}O_{12}Cl$	468.84	174–175	−44 (27°)	−20,630	4	$CHCl_3$
1-Bromo-1′,2,3,4,5,6-hexacetyl-*d*-galactose	[28]	$C_{18}H_{25}O_{12}Br$	513.30	179–181	−79 (27°)	−40,500	4	$CHCl_3$
1-Iodo-1′,2,3,4,5,6-hexaacetyl-*d*-galactose	[28]	$C_{18}H_{25}O_{12}I$	560.30	152–153	−111 (25°)	−62,200	2	$CHCl_3$
Methyl α-*d*-galactopyranoside. H_2O	[4, 29, 33]	$C_7H_{16}O_7$	212.20	110	+179.3	+38,050	9	H_2O
Methyl β-*d*-galactopyranoside	[4, 29, 30, 33]	$C_7H_{14}O_6$	194.18	178	0	0	10	H_2O
Methyl 2,3,4,6-tetraacetyl-α-*d*-galactopyranoside	[32, 33]	$C_{15}H_{22}O_{10}$	362.33	86–87	+133.0	+48,200	3	$CHCl_3$
Methyl 2,3,4,6-tetraacetyl-β-*d*-galactopyranoside	[30, 33]	$C_{15}H_{22}O_{10}$	362.33	93–94	−14.0	−5,070	2	$CHCl_3$
Ethyl *d*-galactofuranoside	[31]	$C_8H_{16}O_6$	208.21	85–86	−102	−21,200	1	H_2O
Methyl 2, 3, 4, 5-tetraacetyl-α-*d*-galactoseptanoside.	[34]	$C_{15}H_{22}O_{10}$	362.33	108	+17.0	+6,160	1	$CHCl_3$
Methyl 2, 6-dimethyl-β-*d*-galactopyranoside.	[8]	$C_9H_{18}O_6$	222.24	45–47	−23.3 (17°)	−5,180	6	$CHCl_3$

Methyl 2, 3, 4-trimethyl-α-*d*-galactopyranoside.	[13]	$C_{10}H_{20}O_6$	236.26	30	+198.4 (25°)	+46,870	1	H_2O
Methyl 2, 3, 4, 6-tetramethyl-β-*d*-galactopyranoside.	[11, 32, 35]	$C_{11}H_{22}O_6$	250.29	46–47	+20.7	+5,100	1	H_2O
Monoacetone-*d*-galactose	[36]	$C_9H_{16}O_6$	220.22	157	−10.9	−2,400	2	EtOH
d-Galactonic acid [4]	[37, 38, 39, 40]	$C_6H_{12}O_7$	196.16	148	−13.6	−2,670		H_2O
d-Galactonic γ-lactone	[37, 38, 40, 41]	$C_6H_{10}O_6$	178.14	{133–135 {110–112	−77.4	−13,790		H_2O
d-Galactonic amide	[42]	$C_6H_{13}O_6N$	195.17	176	+31.8	+6,210	2	H_2O
d-Galactonic phenylhydrazide	[40]	$C_{12}H_{18}O_6N_2$	286.28	203	+10.4	+2,980	2	H_2O (?)
d-Galactal (talal)	[43, 44]	$C_6H_{10}O_4$	146.14	100				

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Rotation 5 minutes after solution.
[3] The alpha-beta nomenclature is opposite to that of Hudson. See footnote 39.
[4] A hydrate ($C_{12}H_{24}O_{14}\cdot H_2O$ mp 140 to 142° C.) crystallizes from aqueous solution.

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-α-GALAHEPTOSE [2]

```
                H    OH   OH   H    H
CH2OH —— C —— C —— C —— C —— C —— CHO
                OH   H    H    OH   OH
```

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
α-*d*-α-Galaheptose.H_2O	[1, 2]	$C_7H_{16}O_8$	228. 20	77–78	−25.2→−14.0	−5, 750	4	H_2O
d-α-Galaheptose phenylhydrazone	[3]	$C_{13}H_{20}O_6N_2$	300. 31	195–205				
d-Galaheptose phenylosazone	[3]	$C_{19}H_{24}O_5N_4$	388. 42	224				
2,3,4,5,6,7-Hexaacetyl-*d*-α-galaheptose	[4]	$C_{19}H_{26}O_{13}$	462. 40	173–174	+27.0	+12, 500	1	$CHCl_3$
1,1′,2,3,4,5,6,7-Octaacetyl-*d*-α-galaheptose	[4]	$C_{23}H_{32}O_{16}$	564. 49	112	+29.8	+16, 800	2	$CHCl_3$
Methyl α-*d*-α-galaheptopyranoside	[2]	$C_8H_{16}O_7$	224. 21	132	−70.2	−15, 700	3	H_2O
Methyl β-*d*-α-galaheptopyranoside	[5]	$C_8H_{16}O_7$	224. 21	Sirup	+74		3	H_2O
Methyl pentaacetyl-α-*d*-α-galaheptopyranoside.	[2]	$C_{18}H_{26}O_{12}$	434. 39	108	−20.4	−8, 860	2	$CHCl_3$
Methyl pentaacetyl-β-*d*-α-galaheptopyranoside.	[5]	$C_{18}H_{26}O_{12}$	434. 39	171–173	+77.6	+33, 700	4	$CHCl_3$
Ethyl α-*d*-α-galaheptopyranoside	[2]	$C_9H_{18}O_7$	238. 24	138	−65.4	−15, 600	2	H_2O
Ethyl pentaacetyl-α-*d*-α-galaheptopyranoside	[2]	$C_{19}H_{28}O_{12}$	448. 42	92	−24.9	−11, 200	4	$CHCl_3$
d-α-Galaheptonic acid	[2, 6, 7]	$C_7H_{14}O_8$	226. 18	143–147	+2.5 [3]→−28. 3		1	H_2O
d-α-Galaheptonic γ-lactone	[2, 3, 6]	$C_7H_{12}O_7$	208. 17	151	−52.3	−10, 900		H_2O
d-α-Galaheptonic amide	[8]	$C_7H_{15}O_7N$	225. 20	206	+14.3	+3, 220	1	H_2O
d-α-Galaheptonic phenylhydrazide	[3, 9]	$C_{13}H_{20}O_7N_2$	316. 31	226	+8.5(80°)	+2, 700	1	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Isbell's nomenclature used.
[3] At 5 minutes and 10 days.

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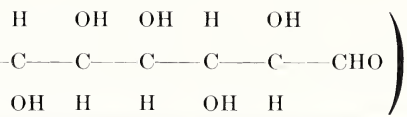
d-β-GALAHEPTOSE [2]



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
β-*d*-β-Galaheptose	[1, 2, 3]	$C_7H_{14}O_7$	210.18	197	−19.2→−54.1	−4,040	4	H_2O
Hexaacetyl-α-*d*-β-galaheptose	[3]	$C_{19}H_{26}O_{13}$	462.40	100–101	−55.8	−25,800	2	$CHCl_3$
Hexaacetyl-β-*d*-β-galaheptose	[3]	$C_{19}H_{26}O_{13}$	462.40	151–152	+30.2	+14,000	2	$CHCl_3$
Methyl α-*d*-β-galaheptopyranoside	[4]	$C_8H_{16}O_7$	224.21	154–155	−108	−24,200	4	H_2O
Methyl β-*d*-β-galaheptopyranoside	[3]	$C_8H_{16}O_7$	224.21	182–183	+36.0	+8,100	2	H_2O
Methyl pentaacetyl-β-*d*-β-galaheptopyranoside	[3]	$C_{18}H_{26}O_{12}$	434.39	122–123	+51.8	+22,500	2	$CHCl_3$
d-β-Galaheptonic amide	[3]	$C_7H_{15}O_7N$	225.20	170–171	−20	−4,500	1	H_2O
d-β-Galaheptonic phenylhydrazide	[3]	$C_{13}H_{20}O_7N_2$	316.31	189–190	−7.8	−2,500	--------	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Isbell's nomenclature used.

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

GENTIOBIOSE (6-(β-*d*-Glucopyranosido)-*d*-glucose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
α-Gentiobiose.2CH_3OH	[1]	$C_{14}H_{30}O_{13}$	406. 38	85–86	+21.4→+8.7	+8, 700	5	H_2O
Gentiobiose phenylosazone	[3]	$C_{24}H_{32}O_9N_4$	520. 53	170–173	−74.8	−38, 940	2	Pyridine+EtOH
Heptaacetyl-α-gentiobiose	[4]	$C_{26}H_{36}O_{18}$	636. 55	178	+35.1 [2]→+31.6	+22, 300	-------	Pyridine
Octaacetyl-α-gentiobiose	[6]	$C_{28}H_{38}O_{19}$	678. 59	189	+52.4	+35, 600	4	$CHCl_3$
Octaacetyl-β-gentiobiose	[2,5,6]	$C_{28}H_{38}O_{19}$	678. 59	193	−5.3	−3, 600	6	$CHCl_3$
1-Fluoro-heptaacetyl-α-gentiobiose	[7]	$C_{26}H_{35}O_{17}F$	638. 54	168–169	+43.8	+28, 000	2	$CHCl_3$
1-Chloro-heptaacetyl-α-gentiobiose	[7]	$C_{26}H_{35}O_{17}Cl$	655. 00	148	+80.5	+52, 700	2	$CHCl_3$
1-Bromo-heptaacetyl-α-gentiobiose	[7]	$C_{26}H_{35}O_{17}Br$	699. 46	144	+101.1	+70, 700	2	$CHCl_3$
1-Iodo-heptaacetyl-α-gentiobiose	[7]	$C_{26}H_{35}O_{17}I$	746. 46	134 d.	+126.1	+94, 100	2	$CHCl_3$
Methyl α-gentiobioside [3]	[8]	$C_{13}H_{24}O_{11}$	356. 32	120	+65.5 (18°)	+23, 340	-------	H_2O
Methyl β-gentiobioside	[6]	$C_{13}H_{24}O_{11}$	356. 32	98	−36.0	−12, 800	8	H_2O
Methyl heptaacetyl-α-gentiobioside	[8]	$C_{27}H_{38}O_{18}$	650. 58	96	+64.5	+42, 000	14	$CHCl_3$
Methyl heptaacetyl-β-gentiobioside	[6]	$C_{27}H_{38}O_{18}$	650. 58	82	−18.9	−12, 300	11	$CHCl_3$
Gentiobial	[4]	$C_{12}H_{20}O_9$	308. 28	194	−5.8 (23°)	−1, 790	2	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] At 3 minutes and 22° C.
[3] Crystallizes with one molecule of C_2H_5OH. Constants are on alcohol-free substance.

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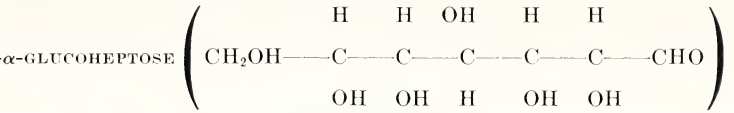
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

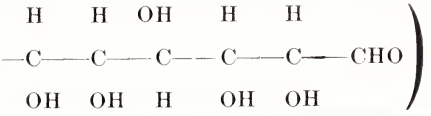
d-α-GLUCOHEPTOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
β-*d*-α-Glucoheptose	[1, 2, 3, 4]	$C_7H_{14}O_7$	210.18	193	−28.7→−20.2	−6,030	4	H_2O.
d-α-Glucoheptose β-naphthylhydrazone.	[2]	$C_{17}H_{22}O_6N_2$	350.36	182	−13 (17°)	−4,550	1	Pyridine.
d-Glucoheptose phenylosazone	[3, 4, 5]	$C_{19}H_{24}O_5N_4$	388.42	194–195	−1→+35.6	−390	2	Pyridine. + EtOH.
4-Methyl-*d*-α-glucoheptose	[6]	$C_8H_{16}O_7$	224.21	185	−26.0→−15.0	−5,830	1	H_2O.
Pentamethyl-α-*d*-α-glucoheptose	[6]	$C_{12}H_{24}O_7$	280.31	80	−8.0→−44.5	−2,240	1	H_2O.
Pentamethyl-β-*d*-α-glucoheptose	[7]	$C_{12}H_{24}O_7$	280.31	84	−62.5→−42.5 (18°)	−17,520	1	H_2O.
Hexaacetyl-α-*d*-α-glucoheptose	[3, 8]	$C_{19}H_{26}O_{13}$	462.40	164	+87.0	+40,230		$CHCl_3$.
Hexaacetyl-β-*d*-α-glucoheptose	[2, 3, 8]	$C_{19}H_{26}O_{13}$	462.40	135	+4.8	+2,220		$CHCl_3$.
1-Chloro-pentaacetyl-α-*d*-α-glucoheptose.	[7]	$C_{17}H_{23}O_{11}Cl$	438.81	97	+95	+41,690	1	$CHCl_3$.
1-Chloro-pentaacetyl-β-*d*-α-glucoheptose.	[7]	$C_{17}H_{23}O_{11}Cl$	438.81	125	+11	+4,830	1	$CHCl_3$.
1-Bromo-pentaacetyl-α-*d*-α-glucoheptose.	[2, 7]	$C_{17}H_{23}O_{11}Br$	483.27	110	+156	+75,390	1	$CHCl_3$.
Methyl-α-*d*-α-glucoheptopyranoside	[9]	$C_8H_{16}O_7$	224.21	106–107	+111.5	+25,000	4	H_2O.
Methyl-β-*d*-α-glucoheptopyranoside	[10]	$C_8H_{16}O_7$	224.21	168–170	−74.9	−16,790	10	H_2O.
Methyl pentaacetyl-α-*d*-α-glucoheptoside.[2]	[7]	$C_{18}H_{26}O_{12}$	434.39	169	+91	+39,530	1	$CHCl_3$.
Methyl pentaacetyl-α-*d*-α-glucoheptoside.[2]	[9]	$C_{18}H_{26}O_{12}$	434.39	174–175	+107.4	+46,650	4	$CHCl_3$.

TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-α-GLUCOHEPTOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
Methyl pentaacetyl-β-*d*-α-glucoheptoside.	[7]	$C_{18}H_{26}O_{12}$	434.39	150	−16	−6,950	1	$CHCl_3$.
1,2-[3,4,6,7-Tetraacetyl-*d*-α-glucoheptose] methyl orthoacetate.	[7]	$C_{18}H_{26}O_{12}$	434.39	112	+43 (17°)	+18,680	1	$CHCl_3$.
d-α-Glucoheptonic acid	[11]	$C_7H_{14}O_8$	226.18		−8.7→−42.4	−1,970	2	H_2O.
d-α-Glucoheptonic γ-lactone	[3, 11, 12]	$C_7H_{12}O_7$	208.17	145–148	−56→−50	−11,660	2	H_2O.
d-α-Glucoheptonic amide	[13, 14]	$C_7H_{15}O_7N$	225.20	134	+10.6	+2,390	1	H_2O.
d-α-Glucoheptonic phenylhydrazide	[15, 16]	$C_{13}H_{20}O_7N_2$	316.31	171–172	+9.3	+2,940	4	H_2O.

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] The difference in structure of these two compounds has not been determined.

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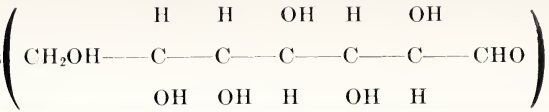
d-β-GLUCOHEPTOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[*M*]	Concentration	Solvent
				°*C*			*g/100 ml*	
d-β-Glucoheptose	[1, 2]	$C_7H_{14}O_7$	210. 19	121	−0.1→ −0.1 [2]	−20	5	H_2O
d-β-Glucoheptose phenylhydrazone	[3]	$C_{13}H_{20}O_6N_2$	300. 31	192				
Hexaacetyl-*d*-β-glucoheptose	[4]	$C_{19}H_{26}O_{13}$	462. 40	136	−9.1	−4, 210	4	$CHCl_3$
d-β-Glucoheptonic acid	[3, 5, 6]	$C_7H_{14}O_8$	226. 18	134–135	+1.3→ −35.5	+300	3	H_2O
d-β-Glucoheptonic γ-lactone	[3, 7]	$C_7H_{12}O_7$	208. 17	161–162	−82.1→ −50.1 [3]	−17, 100	10	H_2O
d-β-Glucoheptonic amide	[8]	$C_7H_{15}O_7N$	225. 20	158	−30.2	−6, 800	5	H_2O
d-β-Glucoheptonic phenylhydrazide	[3]	$C_{13}H_{20}O_7N_2$	316. 31	150–152				

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Complex mutarotation.
[3] Measured at 23° C after heating.

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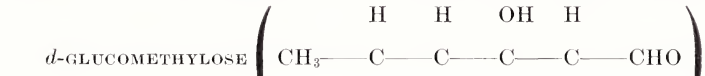
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-GLUCOMETHYLOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
α-*d*-Glucomethylose	[1, 2, 4]	$C_6H_{12}O_5$	164. 16	139–140	+73.3→+29.7	+12, 030	8	H_2O
d-Glucomethylose phenylosazone	[1, 2, 4]	$C_{18}H_{22}O_3N_4$	342. 40	185–187	−94.3 [2]	−32, 290	2	Pyridine
Methyl α-*d*-glucomethylopyranoside	[3]	$C_7H_{14}O_5$	178. 18	98–99				
Methyl β-*d*-glucomethylopyranoside	[4]	$C_7H_{14}O_5$	178. 18	131–132	−55.1	−9, 820	9	H_2O
Methyl triacetyl-α-*d*-glucomethylopyranoside.	[3]	$C_{13}H_{20}O_8$	304. 29	75	+159.2	+48, 440	13	$CHCl_3$
Methyl triacetyl-β-*d*-glucomethylopyranoside.	[4, 5]	$C_{13}H_{20}O_8$	304. 29	94–96	−20.3	−6, 180	8	EtOH
1-Bromo-2,3,4-triacetyl-α-*d*-glucomethylose	[5]	$C_{12}H_{17}O_7Br$	353. 17	135–136	+228.4 (17°)	+80, 660	1	$CHCl_3$
d-Glucomethylonic γ-lactone	[4]	$C_6H_{10}O_5$	162. 14	151–152	+66.9→+5.3	+10, 850	8	H_2O
d-Glucomethylonic phenylhydrazide	[4]	$C_{12}H_{18}O_5N_2$	270. 28	152				

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Measured with white light.

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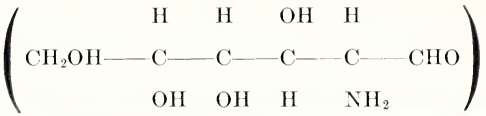
GLUCOSAMINE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C.			g/100 ml	
Pentaacetyl α-glucosamine	[1]	$C_{16}H_{23}O_{10}N$	389. 35	139–140	+93.5	+36, 400	5	$CHCl_3$
Pentaacetyl β-glucosamine	[1]	$C_{16}H_{23}O_{10}N$	389. 35	189	+1.2	+470	4	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

REFERENCES

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-GLUCOSE

```
                H    H    OH   H
CH2OH——C——C——C——C——CHO
                OH   OH   H    OH
```

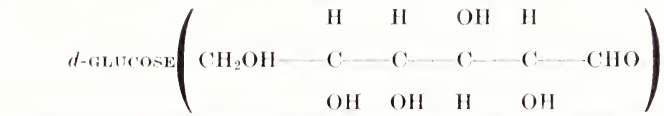
Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
α-*d*-Glucose	[1, 2, 3, 4, 5]	$C_6H_{12}O_6$	180. 16	146	+112.2→+52.7	+20, 210	4	H_2O
α-*d*-Glucose.H_2O	[2, 4]	$C_6H_{14}O_7$	198. 17	83	+102.0→+47.9 [2]			H_2O
β-*d*-Glucose	[1, 4, 6]	$C_6H_{12}O_6$	180. 16	148–150	+18.7→+52.7	+3, 370	4	H_2O
d-Glucose α-phenylhydrazone	[7, 8]	$C_{12}H_{18}O_5N_2$	270. 28	159–160	−87→−50 (approx.)	−23, 510	4	H_2O
d-Glucose β-phenylhydrazone	[7, 8]	$C_{12}H_{18}O_5N_2$	270. 28	140–142	−5→−50 (approx.)	−1, 300	4	H_2O
d-Glucose phenylosazone	[9]	$C_{18}H_{22}O_4N_4$	358. 39	208				
2-Methyl-β-*d*-glucose	[11, 12, 13, 14]	$C_7H_{14}O_6$	194. 18	157–158	+23.5 [3]→+65.3		2	H_2O
3-Methyl-α-*d*-glucose	[15, 16]	$C_7H_{14}O_6$	194. 18	160–161	+104.3→+55.3	+20, 250	1	H_2O
3-Methyl-β-*d*-glucose	[16]	$C_7H_{14}O_6$	194. 18	130–132	+31.9→+55.1	+6, 190	1	H_2O
4-Methyl-*d*-glucose	[10, 12, 17]	$C_7H_{14}O_6$	194. 18	Sirup	? →+53		2	H_2O
5-Methyl-*d*-glucose	[18]	$C_7H_{14}O_6$	194. 18	do	−10.6		2	Ab. EtOH
6-Methyl-α-*d*-glucose	[10, 19, 20]	$C_7H_{14}O_6$	194. 18	145	+110→+55 (16°)	+21, 360	3	H_2O
2,3-Dimethyl-α-*d*-glucose	[16, 21]	$C_8H_{16}O_6$	208. 21	85–87	+81.93→+48.3	+17, 060	1	Acetone
2,3-Dimethyl-β-*d*-glucose	[16, 21]	$C_8H_{16}O_6$	208. 21	108–110	+5.9→+50.9	+1, 230	4	Do.
5,6-Dimethyl-*d*-glucose	[22]	$C_8H_{16}O_6$	208. 21	Sirup	+4.0 (32°)		2	H_2O
3,6-Dimethyl-α-*d*-glucose	[23]	$C_8H_{16}O_6$	208. 21	113–116	+102.5→+61.5 (18°)	+21, 340	3	H_2O
2,3,4-Trimethyl-*d*-glucose	[24, 25]	$C_9H_{18}O_6$	222. 24	Sirup	+50 (approx.)		4	H_2O
2,3,6-Trimethyl-α-*d*-glucose	[26, 27, 28, 29]	$C_9H_{18}O_6$	222. 24	122–123 92–93	+90.2→+70.5			H_2O
2,4,6-Trimethyl-α-*d*-glucose	[30]	$C_9H_{18}O_6$	222. 24	123	+89.7→+71.9	+19, 930	2	H_2O

3,4,6-Trimethyl-*d*-glucose	[31]	$C_9H_{18}O_6$	222.24	Sirup	$+71[\alpha]^{20}_{578}$	----------	2	H_2O
3,5,6-Trimethyl-*d*-glucose	[15, 16]	$C_9H_{18}O_6$	222.24	do	−25.9	----------	1	H_2O
2,3,4,6-Tetramethyl-α-*d*-glucose	[32, 34]	$C_{10}H_{20}O_6$	236.26	88–89	+100.8→+83.3	+23,820	5	H_2O
2,3,4,6-Tetramethyl-β-*d*-glucose	[32]	$C_{10}H_{20}O_6$	236.26	50(Impure)	+73.1→+83.1	----------	5	H_2O
2,3,5,6-Tetramethyl-β-*d*-glucose	[15, 33, 35, 36]	$C_{10}H_{20}O_6$	236.26	Sirup	−28.8	----------	1	$CHCl_3$
3,4,6-Triacetyl-α-*d*-glucose	[37, 38]	$C_{12}H_{18}O_9$	306.27	113–115	+139.6 (18°)	+42,760	2	Ethyl acetate
2,3,4,6-Tetraacetyl-α-*d*-glucose	[39, 40]	$C_{14}H_{20}O_{10}$	348.30	107–108	+138.9	+48,400	1	$CHCl_3$
2,3,4,6-Tetraacetyl-β-*d*-glucose	[41]	$C_{14}H_{20}O_{10}$	348.30	120	+2.2→+82.7	+770	4	EtOH
1,2,3,4-Tetraacetyl-β-*d*-glucose	[42]	$C_{14}H_{20}O_{10}$	348.30	128–129	+12.1	+4,200	6	$CHCl_3$
1,2,3,6-Tetraacetyl-β-*d*-glucose	[42]	$C_{14}H_{20}O_{10}$	348.30	134	−30.2	−10,520	1	H_2O
2,3,4,5,6-Pentaacetyl-*d*-glucose	[43, 44]	$C_{16}H_{22}O_{11}$	390.34	116–118	−4.8 (24°)	−1,870	5	$CHCl_3$
1,2,3,4,6-Pentaacetyl-α-*d*-glucose	[45, 46, 47, 48]	$C_{16}H_{22}O_{11}$	390.34	114	+101.6	+39,700	5	$CHCl_3$
1,2,3,4,6-Pentaacetyl-β-*d*-glucose	[46, 47, 49, 50]	$C_{16}H_{22}O_{11}$	390.34	135	+3.8	+1,480	7	$CHCl_3$
1,1′,2,3,4,5,6-Heptaacetyl-*d*-glucose	[51, 52]	$C_{20}H_{28}O_{14}$	492.43	118–119	+8 (25°)	+3,900	4	$CHCl_3$
1-Chloro-1,2,3,4,5,6-hexaacetyl-*d*-glucose	[53]	$C_{18}H_{25}O_{12}Cl$	468.84	105–106	−49 (25°)	−23,000	4	$CHCl_3$
1-Bromo-1,2,3,4,5,6-hexaacetyl-*d*-glucose	[53]	$C_{18}H_{25}O_{12}Br$	513.30	129–130	−79 (25°)	−40,500	4	$CHCl_3$
1-Fluoro-2,3,4,6-tetraacetyl-α-*d*-glucose.	[54]	$C_{14}H_{19}O_9F$	350.29	108	+90.1	+31,600	3	$CHCl_3$
1-Chloro-2,3,4,6-tetraacetyl-α-*d*-glucose.	[55, 61, 57, 58]	$C_{14}H_{19}O_9Cl$	366.75	75–76	+166.1	+60,900	2	$CHCl_3$
1-Bromo-2,3,4,6-tetraacetyl-α-*d*-glucose.	[58, 59, 60, 61]	$C_{14}H_{19}O_9Br$	411.21	88–89	+197.8	+81,300	2	$CHCl_3$
1-Iodo-2,3,4,6-tetraacetyl-α-*d*-glucose.	[58, 62, 63]	$C_{14}H_{19}O_9I$	458.21	108–109	+237.4	+108,800	2	$CHCl_3$
1-Fluoro-2,3,4,6-tetraacetyl-β-*d*-glucose.	[64]	$C_{14}H_{19}O_9F$	350.29	85–87 98	+19.5 (18°) +21.9 (18°)	+6,800 +7,700	20 10	$CHCl_3$ $CHCl_3$
1-Chloro-2,3,4,6-tetraacetyl-β-*d*-glucose.	[65, 66]	$C_{14}H_{19}O_9Cl$	366.75	99–100	−13.0→+81.2 (17°)	−4,770	1	$CHCl_3$
1-Nitro-2,3,4,6-tetraacetyl-α-*d*-glucose.	[59]	$C_{14}H_{19}O_{11}N$	377.30	150–151	+149.3 (?) (18°)	+56,330	----------	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Calculated from the values for the anhydrous form.
[3] Rotation after 5 minutes

TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-GLUCOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
1-Nitro-2,3,4,6-tetraacetyl-β-*d*-glucose.	[66, 67]	$C_{14}H_{19}O_{11}N$	377.30	96	−8.4	−3,170	1	CCl_4
Pentapropionyl-*d*-glucose	[93]	$C_{21}H_{32}O_{11}$	460.47	Oil	+61.1 (16°)		1	$CHCl_3$
Pentabutyryl-*d*-glucose	[93]	$C_{26}H_{42}O_{11}$	530.60	Oil	+52.0 (16°)		6	$CHCl_3$
Pentapalmityl-α-*d*-glucose	[93, 94]	$C_{86}H_{162}O_{11}$	1,372.17	75	+29.7	+40,750	2	$CHCl_3$
				65–67	+34.3 (16°)	+47,070	4	$CHCl_3$
Pentapalmityl-β-*d*-glucose	[94]	$C_{86}H_{162}O_{11}$	1,372.17	72	+4.6	+6,310	13	$CHCl_3$
Pentastearyl-α-*d*-glucose	[93]	$C_{96}H_{182}O_{11}$	1,512.43	70–71	+34.2 (16°)	+51,730	6	$CHCl_3$
Pentastearyl-β-*d*-glucose	[93, 94]	$C_{96}H_{182}O_{11}$	1,512.43	78	+14.1	+21,330	9	$CHCl_3$
Methyl α-*d*-glucopyranoside	[68, 69, 70, 71]	$C_7H_{14}O_6$	194.18	166	+158.9	+30,860	10	H_2O
Methyl β-*d*-glucopyranoside	[59, 69, 71, 72]	$C_7H_{14}O_6$	194.18	105	−34.2	−6,640	10	H_2O
Methyl tetraacetyl-α-*d*-glucopyranoside.	[47, 55, 59]	$C_{15}H_{22}O_{10}$	362.33	101–102	+130.5	+47,280	4	$CHCl_3$
Methyl tetraacetyl-β-*d*-glucopyranoside.	[47, 59]	$C_{15}H_{22}O_{10}$	362.33	105	−18.2	−6,590	4	$CHCl_3$
Methyl tetramethyl-α-*d*-glucopyranoside.	[32]	$C_{11}H_{22}O_6$	250.29	Sirup	+153.9		12	EtOH
					+147.4		10	H_2O
Methyl tetramethyl-β-*d*-glucopyranoside.	[75, 76, 77]	$C_{11}H_{22}O_6$	250.29	40–41	−17.3	−4,340	4	H_2O
Methyl 2,3,4-trimethyl-β-*d*-glucopyranoside.	[24, 78]	$C_{10}H_{20}O_6$	236.26	93–94	−19.6	−4,630	5	H_2O
					−20.2	−4,770	5	$CHCl_3$
Methyl 2,3,6-trimethyl-β-*d*-glucopyranoside.	[21, 78, 79]	$C_{10}H_{20}O_6$	236.26	59–60	−29.9	−7,060	5	H_2O
					−47.5	−11,220	5	$CHCl_3$

Methyl 2,4,6-trimethyl-β-*d*-glucopyranoside.	[30, 78]	$C_{10}H_{20}O_6$	236.26	70–71	−25.1	−5,930	5	H_2O
					−27.4	−6,470	5	$CHCl_3$
Methyl 3,4,6-trimethyl-β-*d*-glucopyranoside.	[31, 78]	$C_{10}H_{20}O_6$	236.26	52–53	−7.3	−1,720	5	H_2O
					−15.2	−3,590	5	$CHCl_3$
Methyl 2,3-dimethyl-α-*d*-glucopyranoside.	[16]	$C_9H_{18}O_6$	222.24	80–82	+142.6	+31,690	5	H_2O
Methyl 2,3-dimethyl-β-*d*-glucopyranoside.	[78]	$C_9H_{18}O_6$	222.24	62–64	−36.6	−8,130	5	H_2O
Methyl 2-methyl-β-*d*-glucopyranoside.	[78]	$C_8H_{16}O_6$	208.21	97–98	−37.5	−7,810	5	H_2O
Methyl 6-methyl-β-*d*-glucopyranoside.	[80]	$C_8H_{16}O_6$	208.21	133–135	−27.0 (23°)	−5,620	5	H_2O
Methyl α-*d*-glucofuranoside	[81]	$C_7H_{14}O_6$	194.18	62–63	+118	+22,910	5	H_2O
Methyl 5,6-α-*d*-glucofuranoside monocarbonate.	[81]	$C_8H_{12}O_7$	220.18	130	+130 (23°)	+28,620	1	MeOH
Methyl 5,6-β-*d*-glucofuranoside monocarbonate.	[82]	$C_8H_{12}O_7$	220.18	143–145	$-66[\alpha]^{22}_{578}$	----------	1	H_2O
Methyl tetramethyl-α-*d*-glucofuranoside.	[81]	$C_{11}H_{22}O_6$	250.29	11	+102(18°)	+25,530	2	$CHCl_3$
					+107(18°)	+26,780	1	H_2O
Ethyl α-*d*-glucofuranoside	[82]	$C_8H_{16}O_6$	208.21	82–83	+98(23°)	+20,400	2	H_2O
Ethyl β-*d*-glucofuranoside	[81, 82]	$C_8H_{16}O_6$	208.21	59–60	−86(26°)	−17,910	1	H_2O
Ethyl 5,6-α-*d*-glucofuranoside monocarbonate.	[81]	$C_9H_{14}O_7$	234.20	138–140	+117 (17°)	+27,400	1	EtOH
Ethyl 5,6-β-*d*-glucofuranoside monocarbonate.	[82]	$C_9H_{14}O_7$	234.20	164–165	$-50.6\ [\alpha]^{19}_{578}$	----------	1	H_2O
1,2-Monoacetone-*d*-glucose	[83, 84]	$C_9H_{16}O_6$	220.22	161	−11.8	−2,600	8	H_2O
1,2-5,6-Diacetone-*d*-glucose	[69, 84, 85]	$C_{12}H_{20}O_6$	260.28	110–111	−18.5	−4,820	5	H_2O
d-Gluconic acid	[86, 87]	$C_6H_{12}O_7$	196.16	120–131	−6.9	−1,350	5	H_2O
d-Gluconic γ-lactone	[87, 88]	$C_6H_{10}O_6$	178.14	133–135	+68.0	+12,110	5	H_2O
d-Gluconic δ-lactone	[87, 89, 90]	$C_6H_{10}O_6$	178.14	150–152	+66.2	+11,790	5	H_2O
d-Gluconic amide	[91]	$C_6H_{13}O_6N$	195.17	144	+31.2	+6,090	5	H_2O
d-Gluconic phenylhydrazide	[86, 89]	$C_{12}H_{18}O_6N_2$	286.28	200	+12	+3,440	2	H_2O
d-Glucäl	[92]	$C_6H_{10}O_4$	146.14	60	−7.2	−1,050	10	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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323414°—42——48

TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

4-GLUCOSIDO-MANNOSE (4-(β-*d*-glucopyranosido)-*d*-mannose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
4-Glucosido-α-mannose.H_2O	[2, 3]	$C_{12}H_{24}O_{12}$	360. 31	137	+14.7→+5.9	+5, 300	5	H_2O
4-Glucosido-β-mannose	[1]	$C_{12}H_{22}O_{11}$	342. 30	203–205	−6.5→+6.5	−2, 200	3	H_2O
Hexaacetyl-4-glucosido-mannose	[1]	$C_{24}H_{34}O_{17}$	594. 52	171	+21.7	+11, 900	2	$CHCl_3$
Heptaacetyl-4-glucosido-mannose	[1]	$C_{26}H_{36}O_{18}$	636. 55	110	+11.7	+7, 450	5	$CHCl_3$
Octaacetyl-4-glucosido-α-mannose	[4]	$C_{28}H_{38}O_{19}$	678. 59	202–203	+36.2	+24, 600	2	$CHCl_3$
Octaacetyl-4-glucosido-β-mannose	[1]	$C_{28}H_{38}O_{19}$	678. 59	165	−13.0	−8, 820	6	$CHCl_3$
1-Fluoro-heptaacetyl-4-glucosido-α-mannose	[4]	$C_{26}H_{35}O_{17}F$	638. 54	155–156	+13.6	+8, 680	2	$CHCl_3$
1-Chloro-heptaacetyl-4-glucosido-α-mannose	[4]	$C_{26}H_{35}O_{17}Cl$	655. 00	172	+51.2	+33, 500	2	$CHCl_3$
1-Bromo-heptaacetyl-4-glucosido-α-mannose	[4]	$C_{26}H_{35}O_{17}Br$	699. 46	168–169	+77.9	+54, 500	2	$CHCl_3$
1-Iodo-heptaacetyl-4-glucosido-α-mannose	[4]	$C_{26}H_{35}O_{17}I$	746. 46	140	+111.5	+83, 230	2	$CHCl_3$
Methyl 4-glucosido-α-mannopyranoside	[5]	$C_{13}H_{24}O_{11}$	356. 32	227–228	+46 (17°)	+16, 400	1	H_2O
(Methyl 4-glucosido-β-mannopyranoside)$_2$.H_2O.	[1]	$C_{26}H_{50}O_{23}$	730. 66	229	−48.5	[2] −17, 700	4	H_2O
Methyl heptaacetyl-4-glucosido-α-mannopyranoside.	[1, 5]	$C_{27}H_{38}O_{18}$	650. 58	185	+29.3	+19, 100	2	$CHCl_3$
Methyl heptaacetyl-4-glucosido-β-mannopyranoside.	[1]	$C_{27}H_{38}O_{18}$	650. 58	178	−23.2	−15, 100	3	$CHCl_3$
1,2-[Hexaacetyl-4-glucosido-mannose] methyl orthoacetate.	[1]	$C_{27}H_{38}O_{18}$	650. 58	165–167	−13.2	−8, 590	3	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Rotation calculated for one equivalent of the glycoside.

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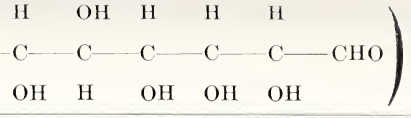
d-α-GULOHEPTOSE [2]



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
α-*d*-α-Guloheptose	[1, 2]	$C_7H_{14}O_7$	210. 18	127	−45.7→−16.9	−9, 610	4	H_2O
d-α-Guloheptonic acid	[1]	$C_7H_{14}O_8$	226. 18	128	−12.6	−2, 850	4	H_2O
d-α-Guloheptonic γ-lactone	[1]	$C_7H_{12}O_7$	208. 17	145	+25.5	+5, 310	4	H_2O
d-α-Guloheptonic phenylhydrazide	[1]	$C_{13}H_{20}O_7N_2$	316. 31	156	+29.3	+9, 270	2	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

[2] Isbell's nomenclature.

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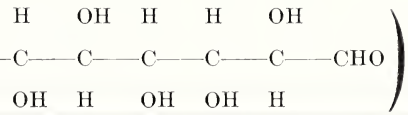
d-β-GULOHEPTOSE [2]



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
α-*d*-β-Guloheptose	[1, 2]	$C_7H_{14}O_7$	210. 18	185–187	−120.5→−65.1	−25, 330	4	H_2O
d-β-Guloheptonic acid	[3]	$C_7H_{14}O_8$	226. 18	135	+12.8	+2, 900	4	H_2O
d-β-Guloheptonic phenylhydrazide	[1]	$C_{13}H_{20}O_7N_2$	316. 31	191–192	−15.4	−4, 870	8	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

[2] Isbell's nomenclature.

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-GULOSE

```
                H     OH    H     H
CH2OH——C——C——C——C——CHO
                OH    H     OH    OH
```

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
α-*d*-Gulose.$CaCl_2$.H_2O	[1, 2]	$C_6H_{14}O_7CaCl_2$	309. 17	205	+37.1→−10	+11, 470	7	H_2O
(*d*-Gulose)$_2$.$CaCl_2$.H_2O	[1]	$C_{12}H_{26}O_{13}CaCl_2$	489. 32	--------	+29.4→−16.5	--------	4	H_2O
d-Gulose phenylhydrazone	[3]	$C_{12}H_{18}O_5N_2$	270. 28	143	--------	--------	--------	
d-Gulose phenylosazone	[4]	$C_{18}H_{22}O_4N_4$	358. 39	160	0→+16 (17°)	0	1	Pyridine+EtOH
Pentaacetyl-*d*-gulose	[5]	$C_{16}H_{22}O_{11}$	390. 34	113	+86.2	+33, 650	4	$CHCl_3$
Methyl α-*d*-gulopyranoside. H_2O	[6]	$C_7H_{16}O_7$	212. 20	77	+109.4	+23, 210	2	H_2O
Methyl monoacetone-α-*d*-guloside	[7]	$C_{10}H_{18}O_6$	234. 25	132–133	+88.5	+20, 730	3	$CHCl_3$
Methyl β-*d*-gulopyranoside	[6]	$C_7H_{14}O_6$	194. 18	176	−83.3	−16, 180	3	H_2O
Methyl tetraacetyl-α-*d*-gulopyranoside.	[6]	$C_{15}H_{22}O_{10}$	362. 33	98	+97.3	+35, 250	3	$CHCl_3$
Methyl tetraacetyl-β-*d*-gulopyranoside.	[6]	$C_{15}H_{22}O_{10}$	362. 33	67	−32.1	−11, 630	3	$CHCl_3$
d-Gulonic γ-lactone	[8, 9]	$C_6H_{10}O_6$	178. 14	182–185	−57.1	−10, 170	4	H_2O
d-Gulonic amide	[10, 11]	$C_6H_{13}O_6N$	195. 17	122–123	+16.1→+13.9	+3, 140	6	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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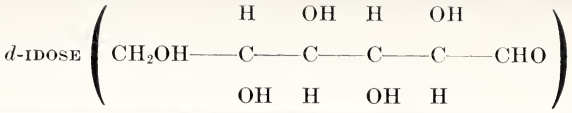
d-IDOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$	$[M]$	Concentration	Solvent
				°C			g/100 ml	
d-Idonic phenylhydrazide	[1]	$C_{12}H_{18}O_6N_2$	286. 28	100–110	−12.4	−3, 550	2	H_2O
d-Idonic acid brucine salt	[1, 2, 4]	$C_{29}H_{38}O_{11}N_2$	590. 61	188	−25.8	−15, 200	2	H_2O
Cadmium *d*-idonate.$CdBr_2.H_2O$	[3]	$C_{12}H_{24}O_{15}Cd_2Br_2$	792. 97	205	−3.2	−2, 540	10	H_2O
Dibenzal-*d*-idonic acid	[2, 5]	$C_{20}H_{20}O_7$	372. 36	227	−57.8	−21, 500	--------	

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

LACTOSE (4-(β-*d*-galactopyranosido)-*d*-glucose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[*M*]	Concentration	Solvent
				°*C.*			*g/100 ml*	
α-Lactose.H_2O	[1, 2, 3, 4]	$C_{12}H_{24}O_{12}$	360. 31	202	+85.0→+52.6	+30, 630	8	H_2O.
β-Lactose	[1, 4]	$C_{12}H_{22}O_{11}$	342. 30	252	+34.9→+55. 4	+11, 950	4	H_2O.
Lactose benzylphenylhydrazone	[5, 6]	$C_{25}H_{34}O_{10}N_2$	522. 54	128	−25.7	−13, 400	1	MeOH
				156–170	−35.4	−18, 500	3	Pyridine.
Lactose phenylosazone	[7, 8]	$C_{24}H_{32}O_9N_4$	520. 53	210–212	−25.4→−7.9 [2]	−13, 200	1	MeOH
Lactose phenylosazone anhydride	[7, 8, 9]	$C_{24}H_{30}O_8N_4$	502. 51	231–232	−147	−73, 900	0. 2	MeOH
Heptaacetyl-β-lactose	[10]	$C_{26}H_{36}O_{18}$	636. 55	83	−0.3(?)	−190	-------	$CHCl_3$
Octaacetyl-α-lactose	[11]	$C_{28}H_{38}O_{19}$	678. 59	152	+53.6	+36, 400	10	$CHCl_3$
Octaacetyl-β-lactose	[11, 12, 13]	$C_{28}H_{38}O_{19}$	678. 59	90	−4.7	−3, 200	10	$CHCl_3$
1-Chloro-heptaacetyl-α-lactose	[14, 15, 16, 17]	$C_{26}H_{35}O_{17}Cl$	655. 00	120–121	+83.9 (22°)	+55, 000	1	$CHCl_3$
1-Bromo-heptaacetyl-α-lactose	[16, 18, 19]	$C_{26}H_{35}O_{17}Br$	699. 46	145 d.	+108.7 (23°)	+76, 030	1	$CHCl_3$
1-Iodo-heptaacetyl-α-lactose	[16]	$C_{26}H_{35}O_{17}I$	746. 46	145 d.	+136.9 (23°)	+102, 200	1	$CHCl_3$
Methyl β-lactoside	[20]	$C_{13}H_{24}O_{11}$	356. 32	170–171	-------	-------	-------	-------
Methyl heptaacetyl-β-lactoside	[19]	$C_{27}H_{38}O_{18}$	650. 58	76–77	−5. 9(19°)	−3, 800	7	$CHCl_3$
Methyl heptamethyl-β-lactoside	[21]	$C_{20}H_{38}O_{11}$	454. 51	77–82	+5.2	+2, 400	1	H_2O
Lactobionic δ-lactone	[22]	$C_{12}H_{20}O_{11}$	340. 28	195–196	+54→+22.3	+18, 380	5	H_2O
Calcium lactobionate-$CaBr_2 6H_2O$	[23]	$C_{24}H_{54}O_{30}Ca_2Br_2$	1062. 67	-------	+18.7	+19, 900	7	H_2O
Lactal	[24, 25, 26]	$C_{12}H_{20}O_9$	308. 28	191–192	+27.5 (23°)	+8, 480	2	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] After 9 hours.

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-LYXOSE

```
                H     OH    OH
CH2OH——C——C——C——CHO
                OH    H     H
```

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
α-*d*-Lyxose	[1, 2, 3, 4]	$C_5H_{10}O_5$	150. 13	106–107	+5.6→−13.8	+840	4	H_2O
β-*d*-Lyxose	[1, 3]	$C_5H_{10}O_5$	150. 13	117–118	−72.6→−13.8	−10, 900	4	H_2O
d-Lyxose *p*-bromphenylhydrazone	[2, 5]	$C_{11}H_{15}O_4N_2Br$	319. 16	156–157	+34.5→+10.0	+11, 000	1	Pyridine.
2,3,4-Trimethyl-α-*d*-lyxose	[6]	$C_8H_{16}O_5$	192. 21	79	−11.9→−21.8 [2]	−2, 300	2	H_2O
Tetraacetyl-α-*d*-lyxose	[7]	$C_{13}H_{18}O_9$	318. 28	93–94	+25 (25°)	+8, 000	--------	$CHCl_3$
1,2-[3,4-Diacetyl-*d*-lyxose] methyl orthoacetate.	[7]	$C_{12}H_{18}O_8$	290. 27	90	−103.5 (22°)	−30, 040	4	$CHCl_3$
Methyl α-*d*-lyxopyranoside	[8, 9]	$C_6H_{12}O_5$	164. 16	108–109	+59.4	+9, 750	5	H_2O
Methyl β-*d*-lyxopyranoside	[10]	$C_6H_{12}O_5$	164. 16	118	−128.1	−21, 030	2	H_2O
Methyl triacetyl-α-*d*-lyxopyranoside	[7, 11]	$C_{12}H_{18}O_8$	290. 27	96	+30.1	+8, 740	1	$CHCl_3$
Methyl triacetyl-β-*d*-lyxopyranoside	[10]	$C_{12}H_{18}O_8$	290. 27	88–89	−109.5	−31, 780	4	$CHCl_3$
Monoacetone-*d*-lyxose	[5]	$C_8H_{14}O_5$	190. 19	79–80	+26.0 (25°)	+4, 940	--------	Acetone.
d-Lyxonic acid	[4, 12]	$C_5H_{10}O_6$	166. 13	--------	+6.6→+52.7 [3]	+1, 100	2	0.1 N HCl
d-Lyxonic lactone	[4, 13, 14]	$C_5H_8O_5$	148. 11	113–114	+81.5	+12, 070	4	H_2O
d-Lyxonic phenylhydrazide [4]	[4, 13, 14, 15]	$C_{11}H_{15}O_5N_2$	256. 26	164	−13.7	−3, 510	4	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] At 1.5 and 28 minutes.
[3] At 11 minutes and 66 days.
[4] Crystallizes as dihydrate, mp 142° C,

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MALTOSE (4-(α-*d*-glucopyranosido)-*d*-glucose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
β-Maltose.H_2O	[1, 2]	$C_{12}H_{24}O_{12}$	360. 31	102–103	+111.7→+130.4	+40, 250	4	H_2O
Maltose β-naphthylhydrazone	[3]	$C_{22}H_{30}O_{10}N_2$	482. 48	176	+10.6	+5, 110	1	MeOH
Maltose phenylosazone	[4, 5]	$C_{24}H_{32}O_9N_4$	520. 53	206	+82.6	+43, 000	2	Pyridine+EtOH
Heptaacetyl-β-maltose	[6, 7, 8]	$C_{26}H_{36}O_{18}$	636. 55	181	+67.8→ +110	+43, 100	--------	$CHCl_3$
Octaacetyl-α-maltose	[9, 11]	$C_{28}H_{38}O_{19}$	678. 59	125	+122.8	+83, 330	5	$CHCl_3$
Octaacetyl-β-maltose	[10, 11]	$C_{28}H_{38}O_{19}$	678. 59	159–160	+62.6	+42, 500	5	$CHCl_3$
1-Fluoro-heptaacetyl-α-maltose	[12]	$C_{26}H_{35}O_{17}F$	638. 54	174–175	+111.1	+70, 940	3	$CHCl_3$
1-Chloro-heptaacetyl-α-maltose	[12, 13, 14]	$C_{26}H_{35}O_{17}Cl$	655. 00	125	+159.5	+104, 500	2	$CHCl_3$
1-Bromo-heptaacetyl-α-maltose	[12]	$C_{26}H_{35}O_{17}Br$	699. 46	112–113	+180.1	+126, 000	2	$CHCl_3$
1-Nitro-heptaacetyl-α-maltose	[15]	$C_{26}H_{35}O_{19}N$	665. 55	93–95	+149.3 (19°)	+99, 370	8	$CHCl_3$
1,2-[Hexaacetylmaltose] orthoacetyl chloride.	[16, 17]	$C_{26}H_{35}O_{17}Cl$	655. 00	112–114	+67.5	+44, 200	13	$CHCl_3$
Methyl β-maltoside [2]	[15, 18, 19, 20]	$C_{13}H_{24}O_{11}$	356. 32	155	+83.9	+29, 900	1	H_2O
Methyl heptaacetyl-β-maltoside	[7, 15, 18]	$C_{27}H_{38}O_{18}$	650. 58	128–129	+53.5	+34, 800	3	$CHCl_3$
1,2-[Hexaacetylmaltose] methyl orthoacetate.	[17]	$C_{27}H_{38}O_{18}$	650. 58	163–164	+101.6 $[\alpha]_{578}$	---------	9	$C_2H_2Cl_4$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Dried over P_2O_5. Compound crystallizes as monohydrate, m.p. 110°C.

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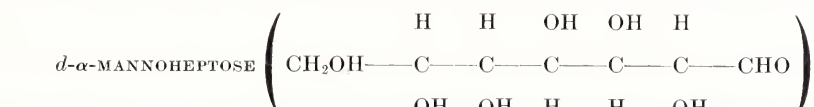
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-α-MANNOHEPTOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
α-*d*-α-Mannoheptose.H_2O	[1, 2]	$C_7H_{16}O_8$	228. 20	107	+120.0→+64.7	+27, 380	4	H_2O
β-*d*-α-Mannoheptose.H_2O	[1]	$C_7H_{16}O_8$	228. 20	104	+42.3→+64.5	+9, 650	4	H_2O
d-α-Mannoheptose phenylhydrazone	[2]	$C_{13}H_{20}O_6N_2$	300. 31	197–200				
d-Mannoheptose phenylosazone	[2]	$C_{19}H_{24}O_5N_4$	388. 42	200	+27.2	+10, 570	1	Acetic acid
Hexaacetyl-α-*d*-α-mannoheptose	[3]	$C_{19}H_{26}O_{13}$	462. 40	75–76	+120.8	+55, 860	1	$CHCl_3$
Hexaacetyl-β-*d*-α-mannoheptose	[3]	$C_{19}H_{26}O_{13}$	462. 40	107	+34.1	+15, 770	1	$CHCl_3$
2,3,4,5,6,7-Hexaacetyl-*d*-α-mannoheptose	[3]	$C_{19}H_{26}O_{13}$	462. 40	146	−34	−15, 700	1	$CHCl_3$
Methyl *d*-α-mannoheptofuranoside	[3]	$C_8H_{16}O_7$	224. 21	115	−111	−24, 900		H_2O
Methyl pentaacetyl-*d*-α-mannoheptofuranoside	[3]	$C_{18}H_{26}O_{12}$	434. 39	76–77	−42.9	−18, 630		$CHCl_3$
d-α-Mannoheptonic acid	[2, 4]	$C_7H_{14}O_8$	226. 18	175	(−)			H_2O
d-α-Mannoheptonic γ-lactone	[2, 4]	$C_7H_{12}O_7$	208. 17	148–150	−74.2	−15, 450	10	H_2O
d-α-Mannoheptonic amide	[5]	$C_7H_{15}O_7N$	225. 20	193–194	+28.0	+6, 310	1	H_2O
d-α-Mannoheptonic phenylhydrazide	[6, 7]	$C_{13}H_{20}O_7N_2$	316. 31	220–223	+21 (80°)	+6, 600	3	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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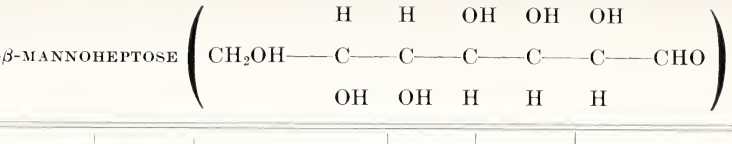
d-β-MANNOHEPTOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
α-*d*-β-Mannoheptose.H_2O	[1, 2]	$C_7H_{16}O_8$	228. 20	83	+45.7→+14.5	+10, 430	4	H_2O
d-β-Mannoheptose *p*-bromophenylhydrazone	[2]	$C_{13}H_{19}O_6N_2Br$	379. 22	191–193				
d-β-Mannoheptonic acid	[1, 2]	$C_7H_{14}O_8$	226. 19	155	+4.0→−25.0	+900	4	H_2O
d-β-Mannoheptonic γ-lactone	[1]	$C_7H_{12}O_7$	208. 17	130	−35.7→−27.9	−7, 430	4	H_2O
d-β-Mannoheptonic phenylhydrazide	[3]	$C_{13}H_{20}O_7N_2$	316. 31	190	−25.8 (27°)	−8, 160	4	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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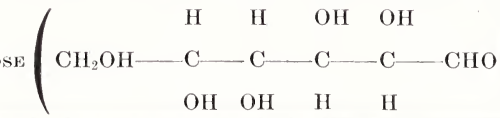
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-MANNOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
α-*d*-Mannose	[1, 2]	$C_6H_{12}O_6$	180. 16	133	+29.3→+14.2	+5, 280	4	H_2O.
β-*d*-Mannose	[1, 3]	$C_6H_{12}O_6$	180. 16	132	−17.0→+14.2	−3, 060	4	H_2O.
d-Mannose.$CaCl_2$.4H_2O	[1, 4]	$C_6H_{20}O_{10}CaCl_2$	363. 22	101–102	−31.3→+6.0 [2]	−11, 370	9	H_2O.
d-Mannose phenylhydrazone	[5, 6]	$C_{12}H_{18}O_5N_2$	270. 28	199–200	+26.3→+33.8 [4]	+7, 110	--------	Pyridine
3,4-Dimethyl-*d*-mannose.H_2O	[7]	$C_8H_{18}O_7$	226. 23	107–109	?→+3	--------	2	H_2O.
3,4,6-Trimethyl-α-*d*-mannose	[8]	$C_9H_{18}O_6$	222. 24	101–102	+21→+8.2 (22°)	+4, 700	1	H_2O.
2,3,4-Trimethyl-*d*-mannose	[7]	$C_9H_{18}O_6$	222. 24	102–103	?→+7	--------	5	H_2O.
2,3,4,6-Tetramethyl-*d*-mannose	[9]	$C_{10}H_{20}O_6$	236. 26	50– 52	+7.4→+2.4	--------	--------	H_2O.
2,3,4,6-Tetraacetyl-*d*-mannose [3]	[10]	$C_{14}H_{20}O_{10}$	348. 30	159–160	−24.2 (19°)	−8, 430	1	$CHCl_3$.
2,3,4,6-Tetraacetyl-*d*-mannose [3]	[11]	$C_{14}H_{20}O_{10}$	348. 30	93	+26. 3 (27°)	+9, 160	1	$CHCl_3$.
1,2,3,4,6-Pentaacetyl-α-*d*-mannose	[12]	$C_{16}H_{22}O_{11}$	390. 34	64	+55.0	+21, 470	4	$CHCl_3$.
1,2,3,4,6-Pentaacetyl-β-*d*-mannose	[13, 16]	$C_{16}H_{22}O_{11}$	390. 34	117–118	−25.2	−9, 840	3	$CHCl_3$.
1,1′,2,3,4,5,6-Heptaacetyl-*d*-mannose.	[14]	$C_{20}H_{28}O_{14}$	492. 43	122	+0.4	+200	--------	$CHCl_3$.
1,2-[3,4,6-triacetyl-*d*-mannose] methyl orthoacetate.	[15]	$C_{15}H_{22}O_{10}$	362. 33	105	−26.6	−9, 640	4	$CHCl_3$.
1-Fluoro-2,3,4,6-tetraacetyl-α-*d*-mannose.	[16]	$C_{14}H_{19}O_9F$	350. 29	68–69	+21.5	+7, 530	2	$CHCl_3$.
1-Chloro-2,3,4,6-tetraacetyl-α-*d*-mannose.	[16, 17]	$C_{14}H_{19}O_9Cl$	366. 75	81	+89.9	+32, 970	2	$CHCl_3$.
1-Bromo-2,3,4,6-tetraacetyl-α-*d*-mannose.	[10, 11, 16]	$C_{14}H_{19}O_9Br$	411. 21	62	+131.6	+54, 120	2	$CHCl_3$.
1-Iodo-2,3,4,6-tetraacetyl-α-*d*-mannose.	[16]	$C_{14}H_{19}O_9I$	458. 21	95	+190.5	+87, 290	2	$CHCl_3$.
Methyl α-*d*-mannopyranoside	[3,18,19]	$C_7H_{14}O_6$	194. 18	193–194	+79.2	+15, 380	1	H_2O.

Methyl β-*d*-mannopyranoside isopropyl alcoholate.	[20]	$C_{10}H_{22}O_7$	254. 23	74–75	−53. 3	−13, 550	4	H_2O.
Methyl tetraacetyl-α-*d*-mannopyranoside.	[15]	$C_{15}H_{22}O_{10}$	362. 33	65	+49.1	+17, 790	4	$CHCl_3$.
Methyl tetraacetyl-β-*d*-mannopyranoside.	[15]	$C_{15}H_{22}O_{10}$	362. 33	161	−50. 4	−18, 260	1	$CHCl_3$.
Methyl tetramethyl-α-*d*-mannopyranoside.	[21, 22]	$C_{11}H_{22}O_6$	250. 29	37–38	+42.9	+10, 740	10	H_2O.
Methyl tetramethyl-β-*d*-mannopyranoside.	[8]	$C_{11}H_{22}O_6$	250. 29	37	−80	−20, 020	1	H_2O.
Methyl α-*d*-mannofuranoside	[23]	$C_7H_{14}O_6$	194. 18	118–119	+113	+21, 940	1	H_2O.
Methyl tetraacetyl-α-*d*-mannofuranoside.	[24]	$C_{15}H_{22}O_{10}$	362. 33	63	+107 (19°)	+38, 770	1	$CHCl_3$.
Methyl tetramethyl-α-*d*-mannofuranoside.	[24]	$C_{11}H_{22}O_6$	250. 29	24	+98.6 (19°)	+24, 680	1	H_2O.
2,3-5,6-Diacetone-*d*-mannose	[25, 26]	$C_{12}H_{20}O_6$	260. 28	122	+11.9→+1.1 [4] (16°)	+3, 100	1	H_2O.
d-Mannonic δ-lactone	[27, 28]	$C_6H_{10}O_6$	178. 14	158–160	+114.8→+30.3 [5]	+20, 450	5	H_2O.
d-Mannonic γ-lactone	[27, 28, 29]	$C_6H_{10}O_6$	178. 14	151–152	+51. 5	+9, 170	5	H_2O.
d-Mannonic amide	[30]	$C_6H_{13}O_5N$	195. 17	173	−17. 3	−3, 380	1	H_2O.
d-Mannonic phenylhydrazide	[31]	$C_{12}H_{18}O_6N_2$	286. 28	214–216	−8.1 (80°)	−2, 320	--------	H_2O.

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Complex mutarotation having maximum value.
[3] The structures of these compounds are open to question. For this reason, they have not been classified as alpha and beta isomers.
[4] Complex mutarotation having minimum value.
[5] Rotation after 2 minutes and 24 hours.

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

MELEZITOSE (glucosido-sucrose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
Melezitose.$2H_2O$	[1, 2]	$C_{18}H_{36}O_{18}$	540. 47	153–154	+88.2	+47, 670	4	H_2O
Hendekaacetylmelezitose	[3, 4]	$C_{40}H_{54}O_{27}$	966. 84	117	+103.6	+100, 160	1	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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MELIBIOSE (6-(α-*d*-galactopyranosido)-*d*-glucose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
β-Melibiose.$2H_2O$	[1, 2]	$C_{12}H_{26}O_{13}$	378. 33	82– 85	+111.7→+129.5	+42, 260	4	H_2O
Melibiose phenylhydrazone	[3]	$C_{18}H_{28}O_{10}N_2$	432. 42	145	----------	----------	--------	
Melibiose phenylosazone	[3, 5]	$C_{24}H_{32}O_9N_4$	520. 53	176–178	+43.2 (21°)	+22, 490	9	Pyridine
Heptaacetyl-β-melibiose	[4]	$C_{26}H_{36}O_{18}$	636. 55	193	+119→+125.8 [2] (24°)	+75, 700	6	$CHCl_3$
Octaacetyl-β-melibiose	[3, 6, 7]	$C_{28}H_{38}O_{19}$	678. 59	177. 5	+102.5	+69, 560	--------	$CHCl_3$
1-Fluoro-heptaacetyl-α-melibiose	[8]	$C_{26}H_{35}O_{17}F$	638. 54	135	+149.7	+95, 590	2	$CHCl_3$
1-Chloro-heptaacetyl-α-melibiose	[8]	$C_{26}H_{35}O_{17}Cl$	655. 00	127	+192.5	+126, 090	2	$CHCl_3$
1-Bromo-heptaacetyl-α-melibiose	[8]	$C_{26}H_{35}O_{17}Br$	699. 46	116	+209.9	+146, 820	2	$CHCl_3$
Methyl heptaacetyl-β-melibioside	[4]	$C_{27}H_{38}O_{18}$	650. 58	158–160	+92.7 (18°)	+60, 310	4	$CHCl_3$
Methyl heptamethyl-β-melibioside	[9]	$C_{20}H_{38}O_{11}$	454. 51	106–107	+97.8	+44, 450	1	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

[2] After 10 minutes and 14 hours.

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NEOLACTOSE (4-(β-*d*-galactopyranosido)-*d*-altrose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$	$[M]$	Concentration	Solvent
				°C			g/100 ml	
β-Neolactose	[1, 2]	$C_{12}H_{22}O_{11}$	342. 30	190	+33.8→+35.5	+11, 570	8	H_2O
β-Neolactose phenylosazone	[3]	$C_{24}H_{32}O_9N_4$	520. 54	195				
Heptaacetyl-α-neolactose	[2]	$C_{26}H_{36}O_{18}$	636. 55	85–95	+23.3→+21.0	+14, 830	8	$CHCl_3$
Heptaacetyl-β-neolactose	[2]	$C_{26}H_{36}O_{18}$	636. 55	135–136	+10.0→+21.0	+6, 370	4–8	$CHCl_3$
Octaacetyl-α-neolactose	[3]	$C_{28}H_{38}O_{19}$	678. 59	178	+53.4(24°)	+36, 240	1	$CHCl_3$
Octaacetyl-β-neolactose	[3]	$C_{28}H_{38}O_{19}$	678. 59	148	−7.1 (24°)	−4, 820	1	$CHCl_3$
1-Chloro-heptaacetyl-α-neolactose	[2, 3]	$C_{26}H_{35}O_{17}Cl$	655. 00	182	+71.2	+46, 640	1	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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[1] H. S. Isbell and W. W. Pigman, heretofore unpublished measurement.
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323414°—42——49

TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

RAFFINOSE (*d*-galactosido-sucrose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
Raffinose.5H_2O	[1, 2, 3]	$C_{18}H_{42}O_{21}$	594. 52	80	+105.2	+62, 540	4	H_2O
Hendecaacetylraffinose	[4, 5]	$C_{40}H_{54}O_{27}$	966. 84	99–101	+92.2	+89, 140	8	EtOH

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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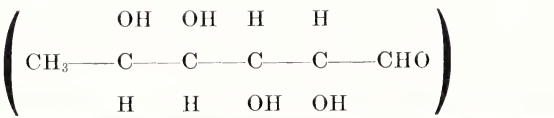
l-RHAMNOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
α-*l*-Rhamnose.H_2O	[1, 2]	$C_6H_{14}O_6$	182. 17	93–94	−8.6→+8.2	−1, 570	4	H_2O
β-*l*-Rhamnose	[3, 4, 5]	$C_6H_{12}O_5$	164. 16	123–125	+38.4→+8. 9	+6, 300		H_2O
l-Rhamnose phenylhydrazone	[6, 7, 8]	$C_{12}H_{18}O_4N_2$	254. 28	158–159	+57.1 [2]→+44.3	+14, 520		H_2O
l-Rhamnose phenylosazone	[9]	$C_{18}H_{22}O_3N_4$	342. 39	222	+94	+32, 200	2	Pyridine.
4-Methyl-β-*l*-rhamnose	[10, 11]	$C_7H_{14}O_5$	178. 18	122	+12.9 (24°)	+2, 300	1	MeOH

3,4-Dimethyl-*l*-rhamnose	[12]	$C_8H_{16}O_5$	192. 21	91–92	−10→+18.6	−1, 920	1	H_2O
5-Methyl-*l*-rhamnose	[11]	$C_7H_{14}O_5$	178. 18	102–103	−4.3 (25°)	--------	3	H_2O
2,3,4-Triacetyl-β-*l*-rhamnose	[13]	$C_{12}H_{18}O_8$	290. 27	96–98	+28.1[3]→−18. 6	+8, 160	8	EtOH
1,2,3,4-Tetraacetyl-β-*l*-rhamnose	[3, 13]	$C_{14}H_{20}O_9$	332. 30	98–99	+13.9	+4, 620	15	$C_2H_2Cl_4$
1,1′,2,3,4,5-Hexaacetyl-*l*-rhamnose	[14]	$C_{18}H_{26}O_{12}$	434. 39	72–73	−7.5 (17°)	−3, 260	--------	MeOH
1,2-[*l*-Rhamnose] methyl orthoacetate	[12, 13]	$C_9H_{16}O_6$	220. 21	140–141	+10 (21°)	+2, 200	1	EtOH
1,2-[3,4-Diacetyl-*l*-rhamnose] methyl orthoacetate.	[12, 13]	$C_{13}H_{20}O_8$	304. 29	83–85	+35.0 (21°)	+10, 650	1	$CHCl_3$
1-Chloro-2,3,4-triacetyl-α-*l*-rhamnose	[15]	$C_{12}H_{17}O_7Cl$	308. 71	73	−127.0	−39, 210	1	$CHCl_3$
1-Bromo-2,3,4-triacetyl-α-*l*-rhamnose	[13]	$C_{12}H_{17}O_7Br$	353. 17	71–72	−169.0	−59, 690	12	$C_2H_2Cl_4$
Methyl α-*l*-rhamnopyranoside	[5, 16]	$C_7H_{14}O_5$	178. 18	109–110	−62.5	−11, 140	10	H_2O
Methyl β-*l*-rhamnopyranoside	[13]	$C_7H_{14}O_5$	178. 18	138–140	+95.4	+17, 000	10	H_2O
Methyl 2,3,4-triacetyl-α-*l*-rhamnopyranoside.	[13, 17]	$C_{13}H_{20}O_8$	304. 29	86–87	−53.7 (16°)	−16, 340	--------	$C_2H_2Cl_4$
Methyl 2,3,4-triacetyl-β-*l*-rhamnopyranoside.	[13]	$C_{13}H_{20}O_8$	304. 29	151–152	+45.7 (18°)	+13, 910	13	$C_2H_2Cl_4$
Methyl 2,3,4-trimethyl-β-*l*-rhamnopyranoside.	[12]	$C_{10}H_{20}O_5$	220. 26	53–54	+106 (21°)	+23, 350	1	H_2O
Methyl 2-acetyl-3,4-dimethyl-β-*l*-rhamnopyranoside.	[12]	$C_{11}H_{20}O_6$	248. 27	67	+36	+8, 940	1	H_2O
Methyl 5-methyl-α-*l*-rhamnofuranoside	[11]	$C_8H_{16}O_5$	192. 21	59–60	−89.2 (23°)	−17, 150	1	H_2O
Monoacetone-*l*-rhamnose-I	[11, 18]	$C_9H_{16}O_5$	204. 22	87–89	+13[4]→+17.8	--------	--------	H_2O
Monoacetone-*l*-rhamnose-II	[11, 19]	$C_9H_{16}O_5$	204. 22	79–80	+10.9[4]→+17.8	--------	4	H_2O
l-Rhamnonic δ-lactone	[20, 21]	$C_6H_{10}O_5$	162. 14	172–182	−100.4	−16, 200	5	H_2O
l-Rhamnonic γ-lactone	[20, 21, 22, 23, 24]	$C_6H_{10}O_5$	162. 14	149–151	−39.2	−6, 360	5	H_2O
l-Rhamnonic amide	[21]	$C_6H_{13}O_5N$	179. 17	134	+27.7	+4, 960	2	H_2O
l-Rhamnonic phenylhydrazide	[23, 25, 26]	$C_{12}H_{18}O_5N_2$	270. 28	195–196	+17.2 (80°)	+4, 650	4	H_2O
l-Rhamnal	[27]	$C_6H_{10}O_3$	130. 14	74. 5	+45.5 (17°)	+5, 920	10	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Rotation after 30 minutes.
[3] Rotation after 10 minutes, in absolute alcohol.
[4] Rotation after 5 minutes.

TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

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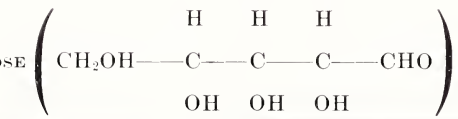
d-RIBOSE



Substance	References	Formula	Molecular	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
d-Ribose	[1, 2]	$C_5H_{10}O_5$	150. 13	87	−23.1→−23.7[2] (1°)	−3, 470	4	H_2O
d-Ribose *p*-bromphenylhydrazone	[2, 3, 4]	$C_{11}H_{15}O_4N_2Br$	319. 17	164	+10.3 (23°)	+3, 290	1	Abs. EtOH
2,3,4-Trimethyl β-*d*-ribose	[5]	$C_8H_{16}O_5$	192. 21	85–86	−51.7→−40.0(27°)	−9, 940	1	H_2O
Tetraacetyl-*d*-ribose	[6]	$C_{13}H_{18}O_9$	318. 28	110	−52.0 (24°)	−16, 550	3	$CHCl_3$
1,2-[Diacetyl-*d*-ribose] methyl orthoacetate	[6]	$C_{12}H_{18}O_8$	290. 26	77–78	+2.4 (26°)	+700	1	$CHCl_3$
1-Bromo-triacetyl-*d*-ribose	[6]	$C_{11}H_{15}O_7Br$	339. 15	96	−209.3 (25°)	−70, 980	2	$CHCl_3$
Methyl *d*-riboside	[7]	$C_6H_{12}O_5$	164. 16	83–84	−113.6	−18, 650	1	H_2O
d-Ribonic lactone	[8]	$C_5H_8O_5$	148. 11	77				

l-RIBOSE

l-Ribose	[1, 9, 10]	$C_5H_{10}O_5$	150. 13	87	+20.3→+20.7 [2]	+3, 050	4	H_2O
l-Ribose *p*-bromphenylhydrazone	[3, 10]	$C_{11}H_{15}O_4N_2Br$	319. 17	164–165	+21.9 (30°)		1	Pyridine
l-Ribonic acid	[11]	$C_5H_{10}O_6$	166. 13	104–105	+17.6→−4.6	+2, 920	3	H_2O
l-Ribonic lactone	[12, 13]	$C_5H_8O_5$	148. 1	79–80	−18.0	−2, 660	9	H_2O
l-Ribonic amide	[14, 15]	$C_5H_{11}O_5N$	165. 15	137–138	−16.4	−2, 710	3	H_2O
l-Ribonic phenylhydrazide	[12]	$C_{11}H_{16}O_5N_2$	256. 26	162–164				

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Complex mutarotation.

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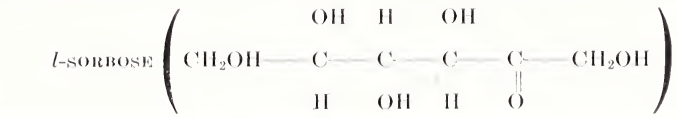
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

l-SORBOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
l-Sorbose	[1, 2, 3]	$C_6H_{12}O_6$	180. 16	159–161	−43.7→−43.4 [2]	−7, 870	12	H_2O
l-Sorbose *p*-bromphenylosazone	[4]	$C_{18}H_{20}O_4N_4Br_2$	516. 20	181				
l-Sorbose phenylosazone	[5]	$C_{18}H_{22}O_4N_4$	358. 39	164	−13 (15°)	−4, 660	1	Pyridine + EtOH
4-Methyl-*l*-sorbose	[6]	$C_7H_{14}O_6$	194. 18	133	?→−30.9 (12°)		2	H_2O
Tetraacetyl-α-*l*-sorbose	[7]	$C_{14}H_{20}O_{10}$	348. 30	100. 8	−21.3	−7, 420	1	$CHCl_3$
Pentaacetyl-α-*l*-sorbose	[7]	$C_{16}H_{22}O_{11}$	390. 34	97	−56.5	−22, 050	1	$CHCl_3$
Pentaacetyl-β-*l*-sorbose	[7]	$C_{16}H_{22}O_{11}$	390. 34	113. 8	+74.4	+29, 040	1	$CHCl_3$
Pentaacetyl-keto-*l*-sorbose	[8, 9]	$C_{16}H_{22}O_{11}$	390. 34	99	+2.8 (λ=578)		5	$CHCl_3$
2-Chloro-tetraacetyl-α-*l*-sorbose	[7]	$C_{14}H_{19}O_9Cl$	366. 75	67	−83.3	−30, 550	1	$CHCl_3$
Methyl α-*l*-sorboside	[7, 10, 11, 12]	$C_7H_{14}O_6$	194. 18	119	−88.7	−17, 200	2	H_2O
Methyl β-*l*-sorboside	[7]	$C_7H_{14}O_6$	194. 18	106. 2	+39.0	+7, 570	2	H_2O
					+84.3	+16, 370	2	MeOH
					+97.1	+18, 850	2	EtOH
					+101.4	+19, 690	1	Ethylacetate.
Methyl tetraacetyl-α-*l*-sorboside	[7]	$C_{15}H_{22}O_{10}$	362. 33	89. 5	−52.6	−19, 060	1	$CHCl_3$
Methyl tetraacetyl-β-*l*-sorboside	[7]	$C_{15}H_{22}O_{10}$	362. 33	75	+79.8	+28, 910	1	$CHCl_3$
Monoacetone-*l*-sorbose	[13]	$C_9H_{16}O_6$	220. 22	92–93				
Diacetone-*l*-sorbose	[13]	$C_{12}H_{20}O_6$	260. 28	77–78	−19	−4, 950	1	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Small complex mutarotation.

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SUCROSE ((*d*-glucopyranosido)-*d*-fructofuranoside)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
Sucrose	[1, 2]	$C_{12}H_{22}O_{11}$	342. 30	188 [2]	+66.53	+22, 770	26	H_2O
Octaacetylsucrose	[3, 4]	$C_{28}H_{38}O_{19}$	678. 59	69 [2]	+59.6	+40, 440	--------	$CHCl_3$
Sucrose octanitrate	[5, 6]	$C_{12}H_{14}O_{27}N_8$	702. 29	85. 5	+55.9	+39, 260	3	MeOH
Octapalmitylsucrose	[7]	$C_{140}H_{262}O_{19}$	2249. 52	54–55	+17.1	+38, 470	4	$CHCl_3$
Octastearylsucrose	[7]	$C_{156}H_{294}O_{19}$	2473. 94	57	+16.6	+41, 070	8	$CHCl_3$
Octacinnamoylsucrose	[8]	$C_{84}H_{70}O_{19}$	1383. 41	87–88	+12.5(18°)	+17, 290	3	$CHCl_3$
Sucrose monophosphate	[9, 10]	$C_{12}H_{23}O_{14}P$	422. 33	Sirup	+85.1	--------	2	H_2O
Heptamethylsucrose	[11]	$C_{19}H_{36}O_{11}$	440. 48	Sirup	+68.5	+30, 170	6	MeOH
Octamethylsucrose	[11, 12]	$C_{20}H_{38}O_{11}$	454. 51	Sirup	+69.3	+31, 500	7	MeOH
Tritritylsucrose	[13]	$C_{69}H_{64}O_{11}$	1069. 21	127–129	+44.3 (23°)	+47, 370	2	EtOH
Pentaacetyl-tritritylsucrose	[13]	$C_{79}H_{74}O_{16}$	1279. 39	125–126	+57 (23°)	+72, 930	1	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.
[2] Crystallized from alcohol. Melting point depends upon solvent used in crystallization, (Helv. Chim. Acta **11**, 901 (1928); **13**, 698 (1930)).

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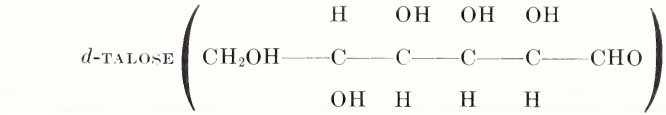
TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-TALOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
α-*d*-Talose	[1, 2, 3]	$C_6H_{12}O_6$	180. 16	133–134	+68.0→+20.8	+12, 250	4	H_2O
β-*d*-Talose	[3]	$C_6H_{12}O_6$	180. 16	120–121	+13.2→+21.0	+2, 380	4	H_2O
d-Talose methylphenylhydrazone	[2, 4]	$C_{13}H_{20}O_5N_2$	284. 31	154				
2,3,4,6-Tetraacetyl-α-*d*-talose	[3]	$C_{14}H_{20}O_{10}$	348. 30	112–113	+42.8	+14, 910	2	$CHCl_3$
1,2,3,4,6-Pentaacetyl-α-*d*-talose	[3]	$C_{16}H_{22}O_{11}$	390. 34	106–107	+70.2	+27, 400	4	$CHCl_3$
1-Bromo-2,3,4,6-Tetraacetyl-α-*d*-talose	[3]	$C_{14}H_{19}O_9Br$	411. 21	84	+165.6	+68, 100	4	$CHCl_3$
1,2-[3,4,6-Triacetyl-*d*-talose] methyl orthoacetate	[3]	$C_{15}H_{22}O_{10}$	362. 33	91. 5–92. 5	+3.7	+1, 340	3	$CHCl_3$
1,2-*d*-Talose orthobenzoic acid	[3]	$C_{13}H_{16}O_7$	284. 26	150–170d.	+21.2	+6, 920	0. 4	H_2O
d-Talonic acid	[5]	$C_6H_{12}O_7.\frac{1}{2}H_2O$	205. 17	138	+19.0 (25°)	+3, 900	4	H_2O
d-Talonic γ-lactone	[5, 6]	$C_6H_{10}O_6$	178. 14	132–134	−34.7 (25°)	−6, 180	2	H_2O
d-Talonic amide	[7]	$C_6H_{13}O_6N$	195. 17	121	−13.1 (25°)	−2, 560	2	H_2O
d-Talonic phenylhydrazide	[8, 9]	$C_{12}H_{18}O_6N_2$	286. 28	159	−25.4 (25°)	−7, 270	3	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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TREHALOSE (α-(α-*d*-glucopyranosido)-*d*-glucopyranoside)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°*C*			*g/100 ml*	
Trehalose.$2H_2O$	[1]	$C_{12}H_{26}O_{13}$	378. 33	97	+178.3	+67, 460	7	H_2O
Hexaacetyltrehalose	[2]	$C_{24}H_{34}O_{17}$	594. 52	93–96	+159 (19°)	+94, 530	3	$CHCl_3$
Octaacetyltrehalose	[3, 4]	$C_{28}H_{38}O_{19}$	678. 59	98	+162.3	+110, 140	10	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

TURANOSE (3-(α-*d*-glucopyranosido)-*d*-fructose)

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	[M]	Concentration	Solvent
				°C			g/100 ml	
Turanose	[1, 2, 7]	$C_{12}H_{22}O_{11}$	342. 30	157	+27.3→+75.8	+9, 340	4	H_2O
Heptaacetylturanose	[3]	$C_{26}H_{36}O_{18}$	636. 55	147	+38.7→+41.7	+24, 630	2	$CHCl_3$
Octaacetylturanose I	[4]	$C_{28}H_{38}O_{19}$	678. 59	216–217	+20. 5	+13, 910	4	$CHCl_3$
Octaacetylturanose II	[4, 5]	$C_{28}H_{38}O_{19}$	678. 59	158	+107.0	+72, 610	1	$CHCl_3$
Octaacetyl-*keto*-turanose III	[4, 6]	$C_{28}H_{38}O_{19}$	678. 59	96	+126.2	+85, 640	6	$CHCl_3$
Octaacetylturanose IV	[4, 5]	$C_{28}H_{38}O_{19}$	678. 59	194–195	+103.2	+70, 030	3	$CHCl_3$
1,2-Turanose methyl orthoacetate	[3]	$C_{15}H_{26}O_{12}$	398. 36	137	+114. 6	+45, 650	1	H_2O
1,2-[Hexaacetylturanose] methyl orthoacetate.	[3]	$C_{27}H_{38}O_{18}$	650. 58	162–164	+80	+52, 050	3	$CHCl_3$
2-Chloro-heptaacetylturanose	[4]	$C_{26}H_{35}O_{17}Cl$	655. 00	165	−0.44	−290	6	$CHCl_3$
2-Bromo-heptaacetylturanose	[4]	$C_{26}H_{35}O_{17}Br$	699. 46	133–134	−30.5	−21, 330	5	$CHCl_3$
2-Iodo-heptaacetylturanose	[4]	$C_{26}H_{35}O_{17}I$	746. 46	105–106	−54. 2	−40, 460	4	$CHCl_3$
Methyl heptaacetyl-β-turanoside	[3]	$C_{27}H_{38}O_{18}$	650. 58	188–189	+27. 5	+17, 890	2	$CHCl_3$

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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d-XYLOSE

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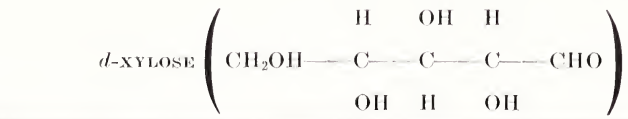
                H     OH    H
CH2OH——C——C——C——CHO
                OH    H     OH
```

Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
α-*d*-Xylose	[1, 2]	$C_5H_{10}O_5$	150. 13	145	+93.6→+18.8	+14, 050	4	H_2O
d-Xylose β-naphthylhydrazone	[3]	$C_{15}H_{18}O_4N_2$	290. 31	124				
d-Xylose phenylosazone	[4, 5]	$C_{17}H_{20}O_3N_4$	328. 36	160–161				
3-Methyl-α-*d*-xylose	[6]	$C_6H_{12}O_5$	164. 16	103–104	+52.2→+14.8	+8, 570	2	H_2O
2-Methyl-β-*d*-xylose	[7]	$C_6H_{12}O_5$	164. 16	132–133	−23.9→+35.9	−3, 920	4	H_2O
Trimethyl-α-*d*-xylose	[8]	$C_8H_{16}O_5$	192. 21	91–92	+64.5→+17.7	+12, 400	1	H_2O
5-Thiomethyl-α-*d*-xylose	[9]	$C_6H_{12}O_4S$	180. 22	74–75	+36.4→+20.6	+6, 560	2	H_2O
2,3,4-Triacetyl-*d*-xylose	[10]	$C_{11}H_{16}O_8$	276. 24	138–141	+70.4→+40. 8(21°)		2	$CHCl_3$
2,3,4,5-Tetraacetyl-*aldehydo*-*d*-xylose	[11]	$C_{13}H_{18}O_9$	318. 28	87–89	−15.9 (26°)	−5, 060	4	$CHCl_3$
1,2,3,4-Tetraacetyl-α-*d*-xylose	[14]	$C_{13}H_{18}O_9$	318. 28	59	+89.3	+28, 400	5	$CHCl_3$
1,2,3,4-Tetraacetyl-β-*d*-xylose	[12, 13, 14]	$C_{13}H_{18}O_9$	318. 28	128	−24.7	−7, 860	5	$CHCl_3$
Hexaacetyl-*d*-xylose	[15]	$C_{17}H_{24}O_{12}$	420. 36	Sirup	+4.0 (17°)			$CHCl_3$
1-Fluoro-2,3,4-triacetyl-α-*d*-xylose	[16]	$C_{11}H_{15}O_7F$	278. 23	87	+67.2	+18, 700	2	$CHCl_3$
1-Chloro-2,3,4-triacetyl-α-*d*-xylose	[14, 17, 18]	$C_{11}H_{15}O_7Cl$	294. 69	105	+171.2	+50, 450	2	$CHCl_3$
1-Chloro-2,3,4-triacetyl-β-*d*-xylose	[19]	$C_{11}H_{15}O_7Cl$	294. 69	112–113	−131.0 (23°)	−38, 600	1	CCl_4
1-Bromo-2,3,4-triacetyl-α-*d*-xylose	[14, 18, 20]	$C_{11}H_{15}O_7Br$	339. 15	101–102	+211.9	+71, 870	2	$CHCl_3$
Methyl α-*d*-xylopyranoside	[21, 22]	$C_6H_{12}O_5$	164. 16	90–92	+153.9	+25, 260	11	H_2O
Methyl β-*d*-xylopyranoside	[21, 22]	$C_6H_{12}O_5$	164. 16	157	−65.5	−10, 750	13	H_2O
Methyl 2,3,4-triacetyl-α-*d*-xylopyranoside	[10]	$C_{12}H_{18}O_8$	290. 27	86	+119.6	+34, 720	4	$CHCl_3$
Methyl 2,3,4-triacetyl-β-*d*-xylopyranoside	[14, 20]	$C_{12}H_{18}O_8$	290. 27	115	−60.8	−17, 650	2	$CHCl_3$

[1] These values are read at 20°C except where the temperature is specified otherwise in parentheses.

TABLE 148.—*Optical rotation and melting point of certain sugars and sugar derivatives*—Continued

d-XYLOSE



Substance	References	Formula	Molecular weight	Melting point	$[\alpha]_D^{20}$ [1]	$[M]$	Concentration	Solvent
				°C			g/100 ml	
Methyl trimethyl-β-*d*-xylopyranoside	[8]	$C_9H_{18}O_5$	206.24	51	−69.5	−14,330	1	$CHCl_3$
Methyl 3,4-dimethyl-β-*d*-xylopyranoside	[7]	$C_8H_{16}O_5$	192.21	89–90	−82.2	−15,800	2	$CHCl_3$
Methyl 2,4-dimethyl-β-*d*-xylopyranoside	[7]	$C_8H_{16}O_5$	192.21	60–61	−82.4	−15,840	1	$CHCl_3$
Methyl 2-methyl-β-*d*-xylopyranoside	[7]	$C_7H_{14}O_5$	178.18	111–112	−67.7	−12,160	1	$CHCl_3$
1,2-Monoacetone-*d*-xylose	[23, 24]	$C_8H_{14}O_5$	190.19	41–43	−19.0 (18°)	−3,610	2–4	H_2O
Diacetone-*d*-xylose	[23, 25]	$C_{11}H_{18}O_5$	230.26	44–45	+13.0 (22°)	+2,990	2	H_2O
d-Xylonic γ-lactone	[26, 27, 28, 29]	$C_5H_8O_5$	148.11	98–101	+91.8	+13,600	5	H_2O
Cadmium *d*-xylonate.$CdBr_2.2H_2O$	[30, 31]	$C_{10}H_{22}O_{14}Cd_2Br_2$	750.93	-------	+8.8	+6,610	1	H_2O
d-Xylonic amide	[32]	$C_5H_{11}O_5N$	165.15	81–82	+44.5 (16°)	+7,350	9	H_2O
d-Xylal (*d*-lyxal)	[33, 34]	$C_5H_8O_3$	116.11	49–50	−254.5 (26°)	−29,550	2	H_2O

[1] These values are read at 20° C except where the temperature is specified otherwise in parentheses.

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TABLE 149.—*Optical rotation and mutarotation of the reducing sugars*

Sugar	Conc.	Temp.	Initial specific rotation	Heat of activation for mutarotation constant [1]		Solvent	Mutarotation: $[\alpha]_D$ at t minutes after solution $= A\times10^{-m_1t}+B\times10^{-m_2t}+{}^2C$					References
				Slow reaction	Fast reaction		Mutarotation constants		Change due to—		Equilibrium rotation	
							Slow reaction	Fast reaction	Slow reaction	Fast reaction		
				Q	Q		${}^3m_1$	${}^3m_2$	A	B	C	
1	2	3	4	5	6	7	8	9	10	11	12	13
	g/100 ml	*° C*	$[\alpha]_D$	*kcal*	*kcal*				$[\alpha]_D$	$[\alpha]_D$	$[\alpha]_D$	
β-l-Arabinose	4.3	20.0	+190.6	16.8	14.7	H_2O	0.0300	0.138	+77.3	+8.8	+104.5	[1]
Do	4.1	0.0	+194.0			H_2O	.00362	.0217	+78.9	+5.9	+109.2	[1]
α-l-Arabinose.$CaCl_2$.$4H_2O$	8.9	20.0	+34.7	16.3	12.1	H_2O	.0300	.169	−16.8	+3.5	+48.0	[1]
Do	9.3	0.0	+35.4			H_2O	.00284	.0369	−16.8	+2.1	+50.1	[1]
α-d-Lyxose	4.0	20.0	+5.6	15.3		H_2O	.0568		+19.4		−13.8	[1]
Do	3.9	0.2	+4.7			H_2O	.00844		+18.1		−13.4	[1]
β-d-Lyxose	4.0	20.0	−72.6	15.7		H_2O	.0591		−58.8		−13.8	[1]
Do	4.0	0.2	−70.8			H_2O	.00840		−57.4		−13.4	[1]
l-Ribose	4.0	20.0	+20.3	15.8	11.7	H_2O	.0492	.231	−7.6	+7.2	+20.7	[1]
Do	4.1	0.2	+23.4			H_2O	.00687	.054	−7.9	+8.1	+23.2	[1]
α-d-Xylose	4.4	20.0	+93.6	16.8		H_2O	.0203		+74.8		+18.8	[1]
Do	4.2	0.0	+95.2			H_2O	.00245		+77.9		+17.3	[1]
α-l-Rhamnose.H_2O	4.0	20.2	−8.6	15.9		H_2O	.0430		−16.8		+8.2	[1]
Do	4.5	0.0	−7.4			H_2O	.00568		−16.1		+8.7	[1]

α-*l*-Fucose	4.0	20.0	−152.6	16.5	--------	H_2O	.0227	--------	−76.7	--------	−75.9	[2]
Do	3.8	0.2	−155.9	--------	--------	Buffer 1 [4]	.00290	--------	−79.2	--------	−76.7	[2]
β-2-Desoxygalactose	3.9	20.1	+40.8	15.6	10.7	Buffer 1 [4]	.0254	.106	−39.0	+19.3	+60.5	[3]
Do	4.0	0.2	+42.5	--------	--------	Buffer 2 [5]	.00359	.0278	−36.4	+11.3	+67.6	[3]
α-*d*-Galactose	5.0	20.0	+150.7	17.3	14.6	H_2O	.00803	.0790	+64.9	+5.6	+80.2	[1]
Do	4.1	0.0	+152.9	--------	--------	H_2O	.000930	.0119	+66.3	+2.7	+84.0	[1]
β-*d*-Galactose	4.0	20.0	+52.8	17.6	14.7	H_2O	.00812	.0883	−32.3	+4.9	+80.2	[1]
Do	4.1	0.0	+55.0	--------	--------	H_2O	.000897	.0167	−31.5	+2.5	+84.0	[1]
α-*d*-Glucose	3.9	20.0	+112.2	17.0	--------	H_2O	.00632	--------	+59.5	--------	+52.7	[1]
Do	3.9	0.2	+111.5	--------	--------	H_2O	.000741	--------	+59.4	--------	+52.1	[1]
β-*d*-Glucose	3.9	20.0	+18.7	17.2	--------	H_2O	.00625	--------	−34.0	--------	+52.7	[1]
Do	3.9	0.2	+18.4	--------	--------	H_2O	.000738	--------	−33.7	--------	+52.1	[1]
α-*d*-Gulose.$CaCl_2$.H_2O	6.81	20.0	+37.1	18.6	--------	H_2O	.0191	--------	+47.1	--------	−10.0	[1]
Do	6.47	0.2	+40.5	--------	--------	H_2O	.00188	--------	+49.9	--------	−9.4	[1]
$(Gulose)_2$.$CaCl_2$.H_2O	4.28	20.1	+29.4	18.2	--------	H_2O	.0197	--------	+45.9	--------	−16.5	[1]
Do	4.21	0.2	+34.6	--------	--------	H_2O	.00202	--------	+51.5	--------	−16.9	[1]
α-*d*-Mannose	4.0	20.0	+29.3	16.7	--------	H_2O	.0173	--------	+15.1	--------	+14.2	[1]
Do	4.0	0.2	+28.8	--------	--------	H_2O	.00216	--------	+14.2	--------	+14.6	[1]
β-*d*-Mannose	4.0	20.0	−17.0	17.1	--------	H_2O	.0178	--------	−31.2	--------	+14.2	[1]
Do	4.0	0.3	−16.7	--------	--------	H_2O	.00214	--------	−31.3	--------	+14.6	[1]
Mannose.$CaCl_2$.$4H_2O$	9.1	20.0	−31.3	17.6	13.0	H_2O	.0245	.311	+4.0	−41.1	+6.0	[1]
Do	8.4	0.0	−29.7	--------	--------	H_2O	.00267	.0608	+4.5	−40.3	+6.2	[1]
α-*d*-Talose	3.8	20.0	+68.0	15.9	12.8	H_2O	0.0263	0.126	+9.3	+37.9	+20.8	[1]
Do	4.0	0.1	+62.5	--------	--------	H_2O	.00362	.0255	+9.8	+27.5	+25.2	[1]
β-*d*-Talose	4.0	20.0	+13.2	16.3	11.5	H_2O	.0262	.101	−17.5	+9.7	+21.0	[4]
Do	3.4	0.1	+13.1	--------	--------	H_2O	.00339	.0241	−17.6	+5.4	+25.2	[4]
α-*d*-α-Galaheptose.H_2O	4.0	20.0	−25.2	--------	--------	H_2O	.00471	--------	−11.2	--------	−14.0	[5]
β-*d*-β-Galaheptose	4.0	20.0	−19.2	--------	--------	H_2O	.00197	--------	+34.9	--------	−54.1	[5]
β-*d*-α-Glucoheptose	4.0	20.0	−28.7	17.3	--------	H_2O	.0080	--------	−8.50	--------	−20.2	[5]
Do	4.0	0.2	−29.0	--------	--------	H_2O	.000933	--------	−6.6	--------	−22.4	[6]
β-*d*-β-Glucoheptose	5.0	20.0	−0.1	16.9	15.6	H_2O	.0108	.050	−11.3	+11.3	−0.1	[7]
Do	7.9	0.3	−1.2	--------	--------	H_2O	.00134	.00728	−10.3	+9.7	−0.6	[6]
α-*d*-α-Guloheptose	4.0	20.1	−45.7	14.2	12.6	H_2O	.0179	.0897	−5.2	−23.6	−16.9	[8]
Do	4.0	0.3	−42.4	--------	--------	H_2O	.00307	.0187	−5.9	−16.3	−20.2	[8]
α-*d*-β-Guloheptose	4.0	20.0	−120.5	--------	--------	H_2O	.00533	.0597	−51.5	−3.9	−65.1	[5]
α-*d*-α-Mannoheptose.H_2O	3.5	20.0	+120.0	--------	--------	H_2O	.00391	.0485	+51.9	+3.4	+64.7	[5]

See footnotes at end of table.

TABLE 149.—*Optical rotation and mutarotation of the reducing sugars*—Continued

Sugar	Conc.	Temp.	Initial specific rotation	Heat of activation for mutarotation constant [1]		Solvent	Mutarotation: $[\alpha]_D$ at t minutes after solution $= A\times10^{-m_1t}+B\times10^{-m_2t}+{}^2C$					References
				Slow reaction	Fast reaction		Mutarotation constants		Change due to—		Equilibrium rotation	
							Slow reaction	Fast reaction	Slow reaction	Fast reaction		
				Q	Q		${}^3m_1$	${}^3m_2$	A	B	C	
1	2	3	4	5	6	7	8	9	10	11	12	13
	g/100 ml	° *C*	$[\alpha]_D$	*kcal*	*kcal*				$[\alpha]_D$	$[\alpha]_D$	$[\alpha]_D$	
β-*d*-α-Mannoheptose.H_2O	4.0	20.0	+42.3			H_2O	.00384	.048	−25.1	+2.9	+64.5	[5]
α-*d*-β-Mannoheptose.H_2O	4.0	20.0	+45.7	16.4	13.2	H_2O	.0141	.0916	+8.3	+22.9	+14.5	[9]
Do	4.0	0.1	+45.1			H_2O	.00181	.0159	+9.3	+19.3	+16.5	[9]
β-Cellobiose	7.7	19.9	+14.2	17.3		Buffer 1 [4]	.00461		−20.4		+34.6	[2]
Do	3.3	0.1	+12.3			do	.000532		−21.5		+33.8	[2]
α-Gentiobiose.2CH_3OH	4.7	20.0	+21.4	16.3		do	.00505		+12.7		+8.7	[2]
Do	4.3	0.2	+22.1			do	.000666		+13.3		+8.8	[2]
α-4-β-Glucosido-mannose.H_2O.	5.4	20.0	+14.6	18.2		H_2O	.0162		+8.7		+5.9	[10]
Do	3.8	0.2	+16.1			H_2O	.00169		+9.5		+6.6	[6]
β-4-β-Glucosido-mannose	3.5	20.0	−6.5			H_2O					+6.5	[11]
α-Lactose.H_2O	7.6	20.0	+85.0	17.3		H_2O	.00471		+32.4		+52.6	[1]
Do	4.9	0.2	+86.4			H_2O	.000544		+32.8		+53.6	[1]
β-Lactose	4.0	20.0	+34.9	17.6		H_2O	.00466		−20.5		+55.4	[1]

Do	3.9	0.2	+36.3			H_2O	.000524		−20.1		+56.4	[1]
β-Maltose.H_2O	4.2	20.0	+111.7	17.5		H_2O	.00527		−18.7		+130.4	[1]
Do	4.5	0.0	+114.8			H_2O	.000580		−16.7		+131.5	[1]
β-Melibiose.2H_2O	4.0	20.0	+111.7	17.2		Buffer 1 [4]	.00863		−17.8		+129.5	[2]
Do	4.0	0.2	+110.5			do	.00101		−17.4		+127.9	[2]
β-Neolactose	7.7	20.0	+33.8	16.3		Buffer 1 [4]	.0203		−1.7		+35.5	[2]
Do	7.5	0.2	+36.1			do	.00268		−1.4		+37.5	[2]
Lactulose	3.9	20.0	−11.9		15.8	Buffer 1 [4]		.0435		+38.8	−50.7	[12]
Do	3.8	0.1	−10.7			do		.00604		+45.9	−56.6	[12]
Levulose	4.0	20.0	−132.2		14.9	Buffer 1 [4]		.0548		−39.8	−92.4	[12]
Do	3.9	0.0	−132.9			Buffer 2 [5]		.00903		−29.5	−103.4	[12]
l-Sorbose	11.3	20.0	−43.7			H_2O	.040	.25	−.86	+.59	−43.4	[13]
Do	11.6	0.4	−43.6			H_2O	.0055	.030	−.55	+.30	−43.3	[13]
Turanose	4.1	20.7	+27.3		14.4	Buffer 2 [5]		.0861		−48.5	+75.8	[12]
Do	3.9	0.2	+27.8			do		.0136		−42.2	+70.0	[12]

[1] Calculated from the integrated Arrhenius equation: $2.3026 \times \log \frac{k_1}{k_2} = \frac{Q}{1.9864}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ and expressed in kilocalories. The values of Q for the slow reaction are calculated from the values of m_1 at approximately 0° and 20° C, while the values of Q for the fast reaction are calculated from the values of m_2 at the same temperatures.

[2] Equilibrium rotation.

[3] Calculated, using logarithms to the base 10.

[4] The solvent was 0.001 *M* acid potassium phthalate solution having a pH of 4.4 at 20° C.

[5] The solvent was prepared by adding 8.0 ml of 0.1064 *N* NaOH to 50 ml of 0.1000 *N* acid potassium phthalate and adding water to make a volume of 1 liter. The pH was 4.6 and the total molarity of the phthalate solution was about 0.005 *M*.

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TABLE 150.—*Corrections to be applied to saccharimetric readings of levulose solutions when a constant normal weight is used*

[Normal weight at 20° C =18.407 g; normal weight at 25° C =19.003 gm]

Polarization [1]	Correction		Polarization [1]	Correction		Polarization [1]	Correction	
	20° C	25° C		20° C	25° C		20° C	25° C
0	0.00	0.00	40	+0.54	+0.57	75	+0.44	+0.47
5	+.10	+.11	45	.56	.60	80	.38	.40
10	.19	.21	50	.57	.61	85	.30	.33
15	.28	.30	52	.58	.61	90	.21	.23
20	.35	.39	55	.57	.61	95	.11	.12
25	.42	.45	60	.56	.59	100	.00	.00
30	.47	.50	65	.53	.56	105	−.11	−.14
35	.51	.55	70	.50	.52	110	−.20	−.26

[1] In order to avoid constant repetition of the negative sign, the polarizations of levulose are considered positive. The positive signs in the above table indicate that the negative polarizations of levulose are to be increased to higher negative values.

XXXVII. APPENDIX 2.—RÉSUMÉ OF THE WORK OF THE INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS

Alexander Herzfeld, chairman; F. G. Wiechmann, American Secretary

FIRST SESSION [1] HAMBURG, GERMANY, JUNE 12, 1897

1. *Kinds of quartz plates to be selected.*—At the start, only quartz plates of high polarizing value shall be tested; later, however, such also as will cover the entire scale range of saccharimeters.

2. *Method of examination of quartz plates.*—Their examination is to be conducted in the same manner as has been done heretofore by the Commission of Trades Chemists under guidance of the Society of the Beet Sugar Industry of the German Empire, with the participation of the Imperial Normal Testing Bureau and the Physical Technical Reichsanstalt.

3. *Temperature to be adopted as the normal temperature for polarization.*—For the examination of quartz plates 20° C is to be chosen as the normal temperature, and the metric liter is to be adopted. The normal weight to be adopted is hence to be 26.00 g, where 26.048 g is the normal weight valid for Mohr's liter at the temperature 17.5° C.

4. *Additional methods and means suggested in order to decrease differences in polarization work.*—In consideration of the well-known difficulties in sampling bagged sugar, sampling each bag does not offer sufficient advantages to justify a departure, in the interests of trade, from the customary method of sampling 20 bags in every 100 bags.

5. *Desirability of an endeavor to introduce uniformity of analytical methods for beet-sugar work in all countries concerned.*—Such an endeavor shall be made. For the computation of sugars, analyses shall be admissible only of such chemists as shall have pledged themselves to execute the analysis of sugar in accordance with the methods prescribed by the International Commission.

6. *The determination of invert sugar.*—The determination of invert sugar is to be made only in solutions which have been clarified with lead solution and from which the lead has then been removed. If volumetric determinations are made, the amount of reduction due to the chemically pure sucrose must be deducted.

SECOND SESSION [2] VIENNA, AUSTRIA, JULY 31, 1898

1. *Results of the international examination of quartz plates.*—In general, such examinations proved satisfactory. Certain discrepancies were undoubtedly due to the fact that the examinations had not always been made at 20° C, as prescribed.

Reference was made to the observations of Herzfeld, Wiechmann, and Wiley that pressures, due to varying temperatures affecting their mountings, exercise an influence on the rotation values of fixedly mounted quartz plates and quartz wedges. Whereas the quartz plates heretofore used—owing to the fact of their being firmly held in their mountings—are apt to be strained when their temperature is raised, and whereas such strains cause irregularities in the polarizing values of these plates, it was resolved that the investigation above referred to should be repeated, making use of other quartz plates not subject to the defect mentioned.

On the motion of Messrs. Dupont and Jobin it was resolved to employ plates the rotation values of which shall cover the entire scale of the saccharimeter, one levorotatory and four dextro-rotatory plates, the thickness of which is at the same time to be given, so that the plates shall remain serviceable when the normal weights shall be changed.

In determining the value of the plates there shall be employed not only the normal temperature of 20° C but, on the motion of Messrs. Wiley and Wiechmann, also of 30° C, in order to take into due account the condition of warmer countries. In employing apparatus with quartz-wedge compensation the changes shall be studied which the saccharimeter itself suffers in consequence of variations of temperature. As source of light there shall be employed only yellow sodium light or light sufficiently purified by ray filters.

Upon the motion of Dr. Hermann, of Hamburg, it was furthermore agreed to emphasize specifically in the protocol that the commission had thus far made no such changes in the normal weight for polariscopes which could influence the results of polarization in the least. This had been mentioned already in the protocol of the Hamburg session of June 12, 1897.

2. *Desirability of examining raw beet sugars for trade purposes according to the inversion method.*—Those present were unanimously of the opinion that the question should, in general, be decided in the negative. Exception should be made only in case of the products obtained in making sugar from molasses; with these it was recommended to make determinations of sugar and of raffinose.

3. *Discussion of applications of the Deutsche Zucker Export Vereine.*—Dr. Hermann suggested that uniformity in analytical methods should even now be striven for as much as possible, and the presiding officer was requested to prepare, with the assistance of the members of the commission, a clear compilation of analytical methods which are in vogue in the different countries, and also to prepare a résumé of the directions which are to be followed in cases of differences in analysis. Basing on these documents, the attempt shall be made to secure international acceptance of a uniform method of procedure.

THIRD SESSION [3] PARIS, FRANCE, JULY 24, 1900

1. *Normal sugar weight to be adopted for saccharimeters of German make when the metric flask is used.*—The Imperial Physical Technical Institute has, by its communication dated October 19, 1898, called attention to the fact that an exact conversion of the normal weight 26.048 g for Mohr's cubic centimeters at 17.5° C corresponds to 26.01 g (not 26.00) metric volume at 20° C, determined in air with brass weights.

The commission decided that in consideration of the insignificance of the deviation the normal weight of 26.00 g shall henceforth be adopted for 100 metric cubic centimeters at 20° C, determined in air with brass weights.

2. *Examination and disposal of quartz plates.*—Prof. Herzfeld reported briefly on the results of the examination of quartz plates, and the commission agreed that these quartz plates should be divided among the nations represented. For the United States, the plates were to be sent to the Department of Agriculture, at Washington; for France, to the Syndicate of Sugar Manufacturers; for Belgium, Holland, Austria-Hungary, and Russia, to the associations of sugar manufacturers represented in the session by delegates.

3. *General principles governing the adjustment of saccharimeters.*—On motion of Messrs. Camuset and Saillard, the following was adopted:

"The convention declares it to be necessary that the rotation of chemically pure sugar be accepted as the fundamental basis in saccharimetry.

"The chemically pure sugar which is to be employed for this purpose shall everywhere be prepared according to the same method, which is as follows (method of the English chemists):

"Purest commercial sugar is to be further purified in the following manner: A hot saturated aqueous solution is prepared and the sugar precipitated with absolute ethyl alcohol, the sugar is carefully spun in a small centrifugal machine and washed in the latter with some alcohol. The sugar thus obtained is redissolved in water, again the saturated solution is precipitated with alcohol, and washed as above. The product of the second centrifugaling is dried between blotting paper and preserved in glass vessels for use. The moisture still contained in the sugar is determined and taken into account when weighing the sugar which is to be used."

The convention furthermore decided that central stations shall be designated in each country which are to be charged with the preparation and the distribution of chemically pure sugar. Wherever this arrangement is not feasible, quartz plates, the values of which have been determined by means of chemically pure sugar, shall serve for the control of saccharimeters.

Mention should be made of the fact that in the discussion on this topic it was remarked, on the one hand, that the preparation of chemically pure sugar is not an easy task, and that in countries having hot climates sugar is dried with difficulty and hence is not stable and hardly available for transportation. Thereupon it was pointed out that the above control, by means of chemically pure sugar, should, as a rule, apply only to the central statio s which are to test the correctness of saccharimeters; for those who execute commercial analyses, the repeated control of the instruments is to be accomplished, now as before, by means of quartz plates.

Concerning the working temperature, the following resolution of Mr. François Sachs was unanimously adopted:

"In general, all sugar tests shall be made at 20° C.

"The adjustment of the saccharimeter shall be made at 20° C. One dissolves (for instruments arranged for the German normal weight) 26.00 g of pure sugar

in a 100-metric cubic centimeters flask,[47] weighing to be made in air, with brass weights, and polarizes the solution in a room, the temperature of which is also 20° C. Under these conditions the instrument must indicate exactly 100.00.

"The temperature of all sugar solutions to be tested is always to be kept at 20° C while they are being prepared and while they are being ploarized.

"However, for those countries the temperature of which is generally higher, it is permissible that the saccharimeters be adjusted at 30° C (or at any other suitable temperature), under the conditions specified above, and providing that the analysis of sugar be made at that same temperature."

Objections were raised against the universal normal weight 20.00 g by Mr. François Sachs as well as by Mr. Strohmer. In consequence, it was resolved not to undertake the introduction of the same, but to adopt the resolution:

"The general international introduction of a uniform normal weight is desirable."

It was furthermore resolved, on the basis of the proposition of Mr. Strohmer, to observe the following rules in raw sugar analysis:

I. POLARIZATION

In effecting the polarization of substances containing sugar, half-shade instruments only are to be employed.

During the operation the apparatus must be in a fixed, unchangeable position, and so far removed from the source of light that the polarizing nicol is not warmed by the same.

As sources of light there are to be recommended lamps with intense flame (gas triple burner with metallic cylinder, lens, and reflector; gas lamp with Auer burner; electric lamp; petroleum duplex lamp; sodium light).

The chemist must satisfy himself, before and after the observation, of the correctness of the apparatus (by means of correct quartz plates) and in regard to the constancy of the light, he must also satisfy himself as to the correctness of the weights, of the polarization flasks, the observation tubes, and the cover glasses. (Scratched cover glasses must not be used.)

Several readings are to be made and the mean thereof taken, but any one individual reading must not be selected.

II. SUGAR ANALYSIS

1. *Sucrose.*—To make a polarization, the whole normal weight for 100 cc is to be used, or a multiple thereof for any corresponding volume.

As clarifying and decolorizing reagents there may be used: Subacetate of lead, prepared according to the German Pharmacopoeia (three parts by weight of acetate of lead, one part by weight of oxide of lead, ten parts by weight of water), Scheibler's alumina cream, concentrated solution of alum. Bone black and decolorizing powders are to be absolutely excluded.

After bringing the solution exactly to the mark and after wiping out the neck of the flask with filter paper, all of the well-shaken, clarified sugar solution is poured upon a dry, rapidly filtering filter. The first portions of the filtrate are to be thrown away and the balance, which must be perfectly clear, is to be used for polarization.

2. *Water.*—In normal beet sugars the water determination is to be made at 105° to 110° C.

For abnormal beet sugars, there is no commercial method for the determination of water.

3. *Ash.*—To determine the ash content in raw sugars the determination is to be made according to Scheibler's method, employing pure concentrated sulphuric acid. For an ash determination at least 3 gr. of the sample are to be used. The incineration is to be carried out in platinum dishes, by means of platinum or clay muffles, at the lowest possible temperature (not above 750° C).

From the weight of the sulphated ash thus obtained 10 percent is to be deducted and the ash content, thus corrected, is to be recorded in the certificate.

4. *Alkalinity.*—As, according to the most recent investigations, the alkalinity of raw sugars is not always a criterion of their durability, the commission abstains from proposing definite directions for the execution of the investigations.

5. *Invert sugar.*—The quantitative determination of invert sugar in raw sugars is to be made according to the method of Dr. A. Herzfeld. (Zeitschrift des Vereins für die Rübenzucker-Industrie des Deutschen Reiches, 1886, pp. 6 and 7.)

Furthermore the following resolutions were adopted.:

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[47] Or during the period of transition, 26.048 g in 100 Mohr's cubic centimeters.

The commission declares that only well-closed glass vessels will insure the stability of samples.

To obtain correct results it is desirable that the samples contain at least 200 gr. of material.

All of the above resolutions were adopted unanimously by those present.

FOURTH SESSION [4] BERLIN, GERMANY, JUNE 4, 1903

1. *Professor Herzfeld outlined the previous work of the commission.*—The sets of quartz plates which had been selected by the Physikalisch-Technische Reichsanstalt in Berlin, and which had been tested in the laboratory of the Verein der Deutschen Zuckerindustrie as to their sugar value, have been distributed to proper central stations of the countries interested, and there kept at the disposal of chemists. These plates have been tested in almost all of the countries which have received the sets, and have been found correct. Some of these stations have thus far not made a report as to the result of this reexamination, and such a report is therefore requested.

Execution of the Paris agreement, according to which chemically pure sugar is to be used for the adjustment of polariscopes and for the testing of plates, has in some countries met with difficulties because they could not succeed in preparing chemically pure sugar. The laboratory at Berlin, therefore, offers to furnish chemically pure sugar.

In the determination of invert sugar a difficulty has arisen, inasmuch as the English chemists have of late again declared against the clarification with basic lead acetate; the commission will therefore have to seek means and methods to prevent, in this respect, loss of uniformity now secured in the methods of analysis.

The day's proceedings furthermore covered reports concerning:

I. Practical experiences made with the uniform methods of analysis agreed upon in Paris.

II. The valuation of "sand" and "krystallzucker" in international trade.

III. Introduction of international uniform directions for sampling raw sugars.

IV and V. Influence of temperature on the specific rotation of sucrose, and introduction of temperature-corrections when the temperature of observation differs from the temperature of 20° C, which has been accepted as the normal temperature.

VI. Determination of the sugar subject to duty or bounty contained in saccharine products and fruit preserves.

VII. Chemical control as an aid to the "entrepôt" system, sanctioned by the Brussels Convention.

FIFTH SESSION [5] BERN, SWITZERLAND, AUGUST 3 AND 4, 1906

1. *The chairman in a review of the achievements of the commission designated the duties of the commission to be purely analytical.*—The commission has for its object the regulation of the methods of sugar analysis and endeavors to secure the working of chemists according to uniform and the best methods, but the commission does not undertake to establish trade customs. The commission does not recognize resolutions carried by majority vote; it is in fact necessary that at least the representatives of the most important countries interested in sugar be in accord on a question before the same is presented for acceptance, as otherwise no reliance can be placed on the recognition of the resolutions by chemists.

2. *Determination of a method of preparing Fehling's solution as well as the manner of making invert-sugar determinations.*—Messrs. Watt and Wiechmann communicated the results of their investigations. Mr. Watt preferred the volumetric method, Mr. Wiechmann the gravimetric method for commercial analyses. The latter moved that clarification with basic lead acetate shall be obligatory for the examination of sirups. This recommendation was indorsed by Messrs. Watt and Prinsen Geerligs and thereupon also by the entire commission.

The chairman reported on tests made for the comparison of Violette's and Fehling's solution, which had not yet been completed. He announced that Mr. Munson, the chairman of the Association of American Agricultural Chemists had, through intervention of Mr. Wiechmann, sent him a resolution of the association named, wherein the same expressed the wish to work hand in hand with the commission in the matter of securing a uniform alkaline copper solution.

Mr. Pellet also presented a paper on this subject, which was published in the Sucrerie Indigène, as well as in the Deutsche Vereinszeitschrift.

Mr. Strohmer promised a later report of his experiments bearing on this question, which are not yet completed. He recommended retaining for the present the so-called Herzfeld method.

Mr. Watt declared himself against basic lead-acetate clarification for solid sugars.

Mr. Sachs refrained from voting.

Mr. Saillard, as well as Mr. Dupont, expressed himself in favor of retaining basic lead acetate clarification as long as the present method was used.

Mr. Pellet declared himself against the use of basic lead acetate as a clarifying reagent.

Mr. Schukow favored this clarification in commercial analysis.

Mr. Watt handed in the following declaration:

"The difference between the amount of the reducing substances in the clarified and the nonclarified solution of beet sugar lies so closely within the limits of the errors of observation that a clarification is unnecessary; but in products which contain a large amount of glucose, a clarification is of great importance."

Mr. Herzfeld was of the opinion that he could not accept the first half of the declaration, the difference being, indeed, a small one, but giving rise to considerable annoyance in trade.

Mr. von Buchka proposed to defer the question of the composition of Fehling's solution and to have the same studied further by a separate commission.

Mr. Geerligs expressed himself in favor of the basic lead-acetate clarification for sirups.

Mr. Main spoke against the basic lead acetate-clarification in raw sugars.

The chairman proposed to request the chemists of Great Birtain to discuss this question in a separate conference once more with delegates of the commission in order to try in this manner to bring about an agreement.

The proposition of the chairman was accepted by the commission and a subcommission was appointed, consisting of Messrs. Strohmer, Saillard, Sachs, Schukow, Van Ekenstein, Watt, Main, Von Buchka, and Herzfeld, this subcommission to take part in the conference with the chemists of Great Britain.

The chairman agreed to ask for the intervention of the German export societies to the end that the conference might soon be called in London.

The question of Fehling's solution should be subjected to further study.

3. *Uniform international directions for sampling sugar products.*

4. *Resolution concerning a uniform form and manner of expression of certificates of analysis for the international sugar trade.*

Mr. Saillard presented the following resolutions:

1. As long as it is not settled that the degree of alkalinity is a sure criterion for the keeping qualities of sugars, the determination of alkalinity shall not be considered in international commerce.

2. The commission shall determine upon a uniform method by which the trade yield (rendement) for the sugar is to be calculated, in establishing scientific molasses coefficients for the impurities (ash and invert sugar) the relation of which is used in the certificates of analysis.

3. The State laboratories shall also take part in the endeavors to bring about uniformity, in order to cause a disappearance of the differences between trade ash determinations and Regie ash determinations. (France.)

These resolutions were accepted by the commission, and the commission also decided, for the present, not to indorse any specific form of certificate of analysis.

5. *Avoidance of the precipitate error in optical sugar analysis.*

6. *Suggestions for the preparation of unchangeable color standards in place of the raw sugar used for the Dutch Standards.*

After a report by the chairman on the substitution of samples of colored glasses for the Dutch standards and a discussion of the question, the commission unanimously expressed the wish that the valuation of sugar according to its color might soon be abandoned altogether, because this practice was to be condemned from the scientific as well as from the practical point of view.

7. *Concerning a method to be recommended for the determination of the sugar content of beets.*—The commission was of the opinion and unanimously adopted the resolution that the aqueous digestion method for the determination of the sugar content of the beets, if it be executed with due regard to the precautions suggested by Pellet, Sachs, and others, was to be recommended in preference to the alcohol method. The commission charged Messrs. Pellet, Sachs, and Herles with presenting detailed working directions of the method.

8. *A uniform international sugar weight.*—After a review by the chairman of the prior discussions on this topic, the introduction by Mr. Dupont of a proposition

to accept 20.00 gr. as the normal weight, and a thorough debate of the proposition, the chairman put the question to those present concerning the desirability of retaining 26.00 gr. as the normal sugar weight for saccharimeters.

Mr. Sachs replied in the affirmative.

Mr. Saillard did not consider it necessary that all countries should have the same normal weight in order to have a uniform method.

On the question being put by the chairman, the representatives present of America, Java, Great Britain, Russia, and Austria-Hungary declared themselves against the normal weight of 20.00 g and for the normal weight of 26.00 g.

Mr. Sachs declared himself in accord with Mr. Saillard to admit 20.00 g, but not to prescribe it.

9. *Conference regarding measures to secure an internationally valid uniform method of beet-seed valuation.*—On the recommendation of the chairman the proposition was accepted that the commission should not occupy itself with the establishment of standards (Normen), but only with the establishment of methods of investigation.

Hereupon a subcommission was chosen to work out uniform methods of examination; Mr. F. Strohmer was appointed chairman of the same.

The following were elected members of the subcommission: Messrs. Strohmer, president; Saillard, Boussaud (Paris), Sachs, Schukow, Müller (Halle), Krüger (Bernburg), Herzfeld, Raatz, von Dippe, Heine, Briem, Neumann, and Herles.

The commission was authorized to increase its numbers by the election of further members.

SIXTH SESSION [6] LONDON, ENGLAND, MAY 31, 1909

1. *Report of the work of the International Commission since its last session.*—Mr. Herzfeld reported that the results of newer investigations speak against the views expressed by the members of the commission in Bern, making obligatory the clarification with basic lead acetate for the determination of invert sugar in sirups. For this reason this matter was therefore that day given place on the program to permit of another resolution. All other resolutions taken in Bern have been put into practice.

Prof. Villavecchia in Rome has agreed, in a letter addressed to the chairman, that the commission shall be called in consultation in case an internationa commission of the Government works out directions for sugar analysis.

Agreeable to the resolution taken in Bern, a compilation of the proceedings to date of the commission has thus far been printed only in German. Copies of this pamphlet will be sent to the members of the commission by the chairman if they so desire. A compilation of the resolution adopted thus far by the commission, which has been prepared by Mr. Wiechmann, of New York, was distributed. Messrs. François Sachs and Saillard promised to publish such a compilation in French.

Mr. Strohmer, Vienna, then reported on the doings of the Subcommission for Uniform Methods of Beet-Seed Analysis, appointed in Bern, which had met under his direction in Vienna on May 24, 1907, but which had taken definite resolutions only with regard to uniform methods for the determination of water and the determination of impurities. A report concerning the session of the subcommission has already been published in the technical journals.

At the suggestion of the referee, the International Commission decided that the introduction of uniform methods of beet-seed examination was to be postponed until it should be settled whether, and in what manner, the present standards (Normen) are to be changed.

2. *Unification of the tables for the calculation of the contents of sugar solutions from their density.*—Messrs. Saillard, Paris, and Von Buchka, Berlin, reported on this topic. Their findings will be published in full in the technical journals.

On the motion of Mr. Sachs, seconded by Messrs. Saillard, Prinsen Geerligs, Strohmer, Neumann, and Pellet, the commission voted unanimously to accept a single table as standard at the temperature of 20° C, which is to be based upon the official German table. From this, other tables may be calculated at other temperatures, for instance, at 15° C, 17.5° C, 30° C, etc., as well as a table according to the Mohr system, 20° C : 20° C.

3. *Propositions for the use of uniform clarifying reagents for the analysis of sugar products.*—Referees: Messrs. Prinsen Geerligs, Java, and François Sachs, Brussels. Their findings will also be published in the technical journals. In this connection Mr. Herles recommended basic lead nitrate as a clarifying reagent.

After an extensive debate in which all delegates took part, the commission unanimously decided that for the direct polarization of solutions of raw sugar products, basic lead acetate shall also in future be used for clarification, but not in excess. For fluid sugars (sirup and molasses) basic lead acetate may not be employed for the determination of invert sugar, but only neutral lead acetate as a clarifying reagent.

An agreement could not be reached concerning the clarifying of solutions of solid raw sugars for the purpose of the determination of invert sugar, as the English chemists remained firm in their former position to effect no clarification whatever for the determination of invert sugar.

4. *Agreement as to a uniform nomenclature for the products of sugar manufacture, especially in view of the food laws.*—Referee: Mr. Strohmer, Vienna, made a report on this topic which will be published in the technical journals. On the motion of the referee and of Messrs Saillard and Silz, a resolution in this matter was, for the present, postponed.

5. Dr. Wiley, of Washington, read two articles by Messrs. A. Hugh Bryan and C. A. Browne, New York, concerning the conditions of basic lead acetate clarification and on temperature corrections in raw-sugar polarizations, which are to be published at once. In consequence of the declaration of Dr. Wiley that in order to avoid temperature corrections the American Government laboratories for sugar analysis are soon to be provided with cooling arrangements in order that the polarizations shall be made exclusively at the normal temperature of 20° C, the commission avoided voting on the resolution of Mr. Browne, New York, in which the avoidance of any and every temperature correction in raw-sugar analysis is demanded. (See article by Mr. Browne in the technical journals.) Prior to this, this resolution has been fully established by Mr. Horne, representing Mr. Browne.

An article by Mr. Horne, on the use of dry basic lead acetate clarification in sugar analysis, could not be read in this session of the commission. This article has been published in the Zeitschrift des Vereins der Deutschen Zucker-Industrie

SEVENTH SESSION [7] NEW YORK, SEPTEMBER 10, 1912

1. *Report on the work done since the last session.*—Mr. Saillard reported that he and Mr. Sachs have conferred about the publication of a compilation of the proceedings of all sessions of the commission in French, and expressed the belief that this will be achieved in time for the next session.

The German Imperial Bureau of Standards (Normaleichungsamt) promised to prepare tables for the determination of the percentage composition of sugar solutions from their specific gravity at different temperatures, as was requested at the London conference.

The following resolution was unanimously adopted:

"Owing to the declaration of Dr. Wiley at the Sixth Session of the International Commission for Uniform Methods of Sugar Analysis, in London, 1909, that, in order to avoid temperature corrections the American Government laboratories for sugar analysis are soon to be provided with cooling arrangements in order that polarizations shall be made exclusively at the normal temperature of 20° C, and to the fact that this declaration has not yet been carried into effect, this commission again expresses the opinion that official polarizations of raw sugar products shall be made only at the constant standard temperature, 20° C, the presence of invert sugar and other impurities precluding the use of formulas and tables, which have been elaborated for correcting the polarization of pure sucrose for changes of temperature."

2. *Uniform methods of sucrose determination in the raw materials of sugar manufacture.*—Mr. Saillard, at the behest of the syndicate of sugar manufacturers, of France, explained that the trade in beets and the trade with molasses does not, for France, bear the same international character as the trade in sugar and requested that the international commission treat analytical methods for beets and molasses only from the viewpoint of analytical chemistry.

Upon the recommendation of Mr. Herzfeld, after a short debate, the commission refrained from officially endorsing uniform methods of sucrose determination in beets and in sugar cane. It was agreed, by publication in the technical journals of the various countries, to bring the reports of Messrs. Strohmer, Sachs, Saillard, Wiechmann, Prinsen Geerligs, and Herles, which were read before the meeting, to the notice of those interested, and to call attention to the propositions of the referees.

3. *Uniform methods for the determination of the specific gravity of sugar solutions.*—Mr. Saillard and Mr. von Buchka presented reports on this topic. These

reports are to be published. Messrs. Weinstein, Strohmer, and Saillard participated in the debate which followed.

It was agreed to publish the reports of the referees, and the following resolutions were adopted. On motion of Mr. Strohmer, that—

"The International Commission for Uniform Methods of Sugar Analysis expresses the wish that the various countries may prescribe a uniform temperature for the density determinations of sugar solutions.

"In trade analyses the use of temperature-correction tables should be dispensed with as far as possible."

On motion of Mr. von Buchka, that—

"The normal temperature of +20° C is to be retained for trade analyses.

"In density determinations of aqueous sugar solutions the density obtained at normal temperature shall be referred to the density of water at +4° C and to vacuo.

"In density determinations made by weighing, the results must be calculated to $\frac{20}{4}$ °C and to vacuo. To effect this, it will be desirable to use tables prepared for the purpose."

Mr. Saillard agreed to the latter part of the resolution, provided that in France the normal temperature there customary—namely, $\frac{15}{4}$ °C—be retained in place of $\frac{20}{4}$ °C.

4. *Resolution concerning a further examination of the inversion constants of the double polarization (Clerget-Herzfeld) method.*—Mr. Herzfeld reported that although the correctness of the constant, 132.66 at 20° C, for a solution which contains the German half-normal weight of pure sucrose, has been confirmed by numerous chemists and, finally, by an international commission of chemists, who worked in Berlin in 1910, yet, on the basis of more recent investigations, it seems to him desirable to retest the accuracy of this constant in as far as its application in the analysis of beet molasses is concerned. A committee, consisting of Messrs. Bates, Bryan, Browne, Prinsen Geerligs, Saillard, Sachs, and Strohmer, is appointed to retest this constant.

The following reports were also made and the following resolutions adopted:

Mr. A. Hugh Bryan made a report on the necessity of using light-ray filters for polarizing high-grade sugars, and, on his motion, the following resolution was adopted:

"Wherever white light is used in polarimetric determinations, the same must be filtered through a solution of potassium dichromate of such a concentration that the percentage content of the solution multiplied by the length of the column of the solution in centimeters is equal to nine."

Furthermore, Mr. Bates reported on investigations [8] conducted by the Bureau of Standards which led to the conclusion that the 100 point of saccharimeters provided with Ventzke scales at present accepted is not quite correct. On his motion the following resolution was adopted:

"Inasmuch as recent investigations tend to question the validity of the present 100° point of saccharimeters, and inasmuch as it is desirable that the commission recognize and fix a transformation factor from absolute degrees to Ventzke degrees, the chairman is hereby empowered to appoint a committee of three to fully investigate this question and report at the next official meeting."

At the suggestion of the chairman, Messrs. Bates, Schönrock, and Strohmer were elected as members of this subcommittee.

EIGHTH SESSION, [9] AMSTERDAM, 1932

Frederick Bates, president; Louis Eynon, secretary

Owing to world events, the Commission did not function during the years 1912 to 1932. During this time, many of the delegates in attendance at the seventh session, including the president, Alexander Herzfeld, and the secretary, F. G. Wiechmann, passed away. However, the Commission was reconvened in the Great Senate Room of the University of Amsterdam on September 5, 1932. Much preparatory work, undertaken chiefly on the initiative of Frederick Bates, of the National Bureau of Standards of the United States, had been necessary to insure its success. The first order of business was the adoption of a constitution and by-laws and the Commission, for the first time in its history, had a definite rule of procedure. The following were elected officers of the Commission: presi-

dent, Frederick Bates; vice presidents, E. Saillard, O. Spengler, V. Stanek, M. G. Wagenaar Hummelinck; treasurer, F. Tödt; and secretary, L. Eynon. The session, lasting 4 days, was conducted in English, French, and German.

The following subjects comprised the agenda of the session.

SUBJECT 1.—*The 100° S point of the saccharimeter*

Referee, FREDERICK BATES

Among the recommendations adopted were the following:

"(a) That the Commission adopt a standard scale for the saccharimeter and that this scale be known as the "International Sugar Scale." Rotations expressed in this scale shall be designated as degrees sugar (° S)."

"(b) That the polarization of the normal solution (26.000 g of pure sucrose dissolved in 100 ml of solution) and polarized at 20° C in a 200-mm tube, using white light and the dichromate filter, as defined by the Commission, be accepted as the basis of calibration of the 100° (S) point on the International Sugar Scale."

* * * * * * *

"(h) That the question of the French Scale be held in abeyance."

SUBJECT 2.—*Values of Clerget divisors for the more widely used inversion methods*

Referee, F. W. ZERBAN

The referee recommended that study be made of (1) the Clerget methods used in the various countries, (2) the effect of ash on the Clerget divisor, and (3) the temperature coefficients of the inversion constants.

SUBJECT 3.—*Conductometric determination of the ash content of raw sugars*

Referee, O. SPENGLER

The report of the referee reviewed the subject of conductivity ash and recommended further study, particularly with respect to low-grade products, details of the methods being left to the various countries.

SUBJECT 4.—*Errors due to the volume of lead precipitate in testing raw sugars for polarization*

Referee, H. MAIN

The referee recommended that further studies be made using sugar from all countries. In the meanwhile, the use of Horne's dry lead was permitted.

SUBJECT 5.—*Estimation of reducing sugars and the influence of overheating on the estimation of invert sugar*

Referee, L. EYNON

The recommendation of the referee that ten widely used methods be subjected to study was agreed to. It was further agreed to study methods of estimating the cuprous oxide.

SUBJECT 6.—*Refining and keeping qualities of raw cane and beet sugar*

Referee, H. C. PRINSEN GEERLIGS

It was recommended that no resolution be adopted.

SUBJECT 7.—*Standardization of quartz control plates*

Referee, O. SCHÖNROCK

The referee presented resolutions containing detailed specifications for saccharimeter quartz control plates, including tests for optical purity, plane parallelism, axis error, mounting, rotation, etc.

The Commission agreed to the resolutions presented.

SUBJECT 8.—*Refractometric estimation of water in sugars and sugar products*

Referee, H. MAIN

No definite recommendations were made, the subject being referred to the next session of the commission.

SUBJECT 9.—*Colorimetry in the sugar industry*

Referee, V. SAZAVSKY

It was recommended that the subject be investigated before the next session and that such investigations should include sulfitation products.

SUBJECT 10.—*The testing of molasses*

Referee, E. SAILLARD

The referee recommended detailed study of the various methods.

SUBJECT 11.—*Estimation of raffinose*

Referee, J. VONDRAK

The following resolution was agreed to: It is recommended that the method of Paine and Balch should be studied, the influence of salts being taken into consideration, the method of inversion with acids not being sufficiently accurate. Creydt's mucic-acid method is also recommended for study.

SUBJECT 12.—*Marc volume correction in the digestion process for the estimation of sugar in beet roots*

Referee, V. STANEK

The referee showed that since the volume of the marc varies according to the country, or even district, in which the beet is grown it would be impossible to make any estimate of general applicability.

SUBJECT 13.—*Estimation of sulfur dioxide in consumption sugar*

Referee, J. VONDRAK

The referee recommended the direct titration with iodine for factory control of sulfur dioxide in sugar products. For exact estimation he proposed that the sulfur dioxide be distilled from the acidified solution after expulsion of the air with carbon dioxide; the distillate collected in hydrogen peroxide, bromine water, iodine solution, or in sodium bicarbonate solution with subsequent oxidation, the sulfuric acid formed being estimated gravimetrically.

Amendment of Resolution passed at the Third Session of the Commission (Paris, 1900).

The meeting agreed to a resolution, proposed by F. W. Zerban, to amend the "Directions for Sugar Analysis," subhead 1, adopted at the Third Session of the Commission held in Paris in 1900, to read as follows:

"*Single polarization.*—To make a polarization, the whole normal weight for 100 ml shall be used or a multiple or fraction thereof for any corresponding volume. As clarifying and decolorizing reagents there may be used lead subacetate solution or Horne's dry subacetate of lead and salt-free alumina cream. Bone black and decolorizing powders are excluded.

After bringing the solution exactly to the mark and after wiping out the neck of the flask with filter paper, all of the well-shaken clarified sugar solution is poured upon an air-dry, rapidly filtering filter. During the filtration, the funnel shall be covered with a watch glass or plate to prevent evaporation. At least the first 25 ml of the filtrate is to be thrown away and the remainder, which must be perfectly clear, is to be used for polarization."

NINTH SESSION [10] LONDON, 1936

FREDERICK BATES, president; LOUIS EYNON, secretary

The ninth session, held in London, August 31 to September 3, 1936, was marked by a record attendance of delegates from 20 different countries. The complete

proceedings of the session have been published as a supplement of the International Sugar Journal and reprinted in several of the sugar journals of other countries, making it available in various languages.

Space permits only a résumé of the subjects covered at the meeting.

SUBJECT 1.—*Constitution and bylaws*

Referee, FREDERICK BATES

The president presented a report on proposed amendments, and it was agreed to adopt the "Constitution and Bylaws."

SUBJECT 2.—*Weighing, taring, sampling, and classification of sugars*

Referee, J. VONDRAK

The report of the referee covered the details of the methods employed in the various countries.

SUBJECT 3.—*Conductometric determination of the ash content of raw sugars*

Referee, O. SPENGLER

The report pointed out the advantages of the conductometric method due to the rapidity of execution and simplicity as well as the fact that it gives only the percentage of soluble ash. The suggestion was made that the differences between the gravimetric and conductometric ash be submitted to further study.

SUBJECT 4.—*Determination of reducing sugars and the influence of overheating on the determination of invert sugar*

Referee, J. H. LANE

The methods employed in the various countries were discussed in detail in the report. It was recommended that comparative determinations be made by the Munson and Walker method, Lane-Eynon, and Schoorl methods, and by the Brown, Morris, and Miller method, with particular regard to the concordance obtainable by different chemists using the same method.

The subject of defecation of cane molasses for invert-sugar determinations was recommended for review.

SUBJECT 5.—*Determination of the decolorizing and filtering quality of chars*

Referee, K. SMOLENSKI

The referee reviewed the subject of standardization of tests for the decolorizing power of carbons. It was suggested that a special committee devise standardized methods for the evaluation of activated carbons used in the sugar industry.

SUBJECT 6.—*Testing of molasses*

Referee, E. SAILLARD

The referee reported on a number of methods employed in the analysis of molasses with particular reference to the determination of sucrose in beet molasses. In view of the need of standard methods for various types of molasses, the methods of the National Bureau of Standards were proposed and adopted as tentative.

SUBJECT 7.—*Application of refractometer methods to sugar analysis*

Referee, E. LANDT

On the recommendation of the referee, a standard scale of refractive indices of sucrose solutions at 20° C was adopted, together with a table of temperature corrections. They were designated "International Scale (1936) of Refractive Indices of Sucrose Solutions at 20° C," and the "International Temperature Correction Table (1936)." A corresponding scale for use with the tropical model refractometer at 28° C and a temperature correction table at 28° C were also adopted.

SUBJECT 8.—*The 100° S point of the saccharimeter*

Referee, FREDERICK BATES

In the report presented by the referee and written jointly by him and Francis P. Phelps, it was shown that two different saccharimeter scales are in general use. They are the French Scale and the International Sugar Scale, adopted by the Commission at the eighth session at Amsterdam. The former is used largely in France and the French colonies. It was shown that by taking the original data of the French investigators and recalculating the normal weight for the French Scale the correct value was 16.269 g instead of 16.29 g. The new value, 16.269 g, is in exact agreement with the value of the International Sugar Scale.

SUBJECT 9.—*Standardization of quartz control plates*

Referee, E. EINSPORN

The referee expressed his thanks to Prof. Dr. Schönrock, his predecessor, who had reported on the conditions of testing quartz plates at the eighth session. The referee limited his report to a detailed discussion of the following questions:

(1) Optical purity.
(2) Identification marks.
(3) Plate mounting.
(4) Rotation measurements.
(5) International exchange of quartz control plates.

SUBJECT 10.—*Test for the evaluation of the refining qualities of raw cane and beet sugar*

Referee, O. SPENGLER

The report pointed out that in judging the refining qualities, a distinction must be made between cane and beet raw sugars. Methods applicable to both were discussed and recommended for use.

SUBJECT 11.—*Elimination of errors due to lead clarification in polarizing raw sugars*

Referee, K. SANDERA

The report of the referee cited various investigations regarding the difference in polarization after wet and dry lead clarification. After a long discussion, the following recommendation was considered and adopted:

"If no change in the sugar scale is or has been made, clarification shall be effected with standard lead subacetate solution (3d Session Int. Comm. Paris, 1900); but if a change from the Herzfeld-Schönrock scale to the International Sugar Scale is made, then clarification shall be effected with standard dry lead subacetate (Horne's dry lead)."

SUBJECT 12.—*The determination of raffinose*

Referee, J. VONDRAK

In comparing the rapid optical method of Osborn and Zisch with the enzyme method of Paine and Balch, the referee considered that the close agreement obtained on products from American beet-sugar factories could be explained only by the compensation of the rotation of particular nonsugars, since these substances are far from being optically inactive, even in acid solution. It was further stated that the method of Osborn and Zisch or any new method for the determination of raffinose must be judged by its capacity to give results always in close agreement with those obtained by the basic methods, working with enzymes.

SUBJECT 13.—*Colorimetry in the sugar industry*

Referee, V. SAZAVSKY

In the referee's report which was adopted, it was recommended that absolute measurement be introduced as far as possible into factory and commercial control. It was suggested that the program of the section be extended to include the measurement of turbidity and reflection.

SUBJECT 14.—*Values of Clerget divisors for the more widely used inversion methods*

Referee, F. W. ZERBAN

The work of a number of investigators was covered in the report of the referee. The lack of sufficient analytical data caused the referee to recommend the following:

"It is recommended that the resolution adopted at the eighth session be repeated, and that a further study be made of the three subjects mentioned therein."

This recommendation was agreed to by the Commission.

SUBJECT 15.—*Determination of water in sugars and sugar products by drying methods*

Referee, H. C. S. DE WHALLEY

The report of the referee covered a number of the methods in use in the various countries. Included in the methods recommended and adopted were the following:

"(1) That the standard method for moisture in refined sugars and normal raws should be carried out in a vacuum oven at 60° C, pressure not exceeding 5 cm, oven bled with current of dry air, drying to constant weight, and dishes to be metal with close-fitting lids with knobs.

"(2) That the standard method for estimation of water in beet molasses, low-ash cane sirups, and golden sirups, should be carried out in vacuum ovens bled with dry air at 70° C, or preferably 60° C, with a pressure not exceeding 5 cm; metal dishes with close-fitting lids with knob should be used and that with 1 g of solids approximately 25 to 30 g of 40 to 60 mesh white quartz sand should be used; water being added to facilitate admixture with the sand and then drying until 2 hourly weighings do not differ by 0.5 mg."

SUBJECT 16.—*Determination of the hydrogen-ion concentration of sugar-factory products*

Referee, K. SMOLENSKI

It was agreed to defer this subject until the next session of the Commission.

SUBJECT 17.—*Analysis and evaluation of refined sugars*

Referee, K. SANDERA

The report of the referee showed the lack of uniformity in the tests made in the various countries in the evaluation of refined sugar, and gave a detailed discussion of some of the methods. He suggested that a selection be made of the tests most widely used in the evaluation of refined sugars, that these tests be investigated, and that recommendations be drawn up for carrying them out in a uniform manner.

1. REFERENCES

[1] F. C. Wiechmann, Sugar Analysis, p. 217 (John Wiley & Sons, Inc., New York, N. Y., 1914); Z. Ver. deut. Zucker-Ind. **47,** pt. 1, 235 (1897).
[2] Z. Ver. deut. Zucker-Ind. **48,**, pt. 1, 389 (1898).
[3] Z. Ver. deut. Zucker-Ind. **50,** pt. 1, 357 (1900).
[4] Z. Ver. deut. Zucker-Ind. **53,** pt. 2, 889 (1903).
[5] Z. Ver. deut. Zucker-Ind. **56,** pt. 2, 317 (1906); **57,** pt. 1, 6 (1907); Int. Sugar J. **9,** 5 (1907).
[6] Z. Ver. deut. Zucker-Ind. **59,** pt. 1, 434 (1909); Int. Sugar J. **11,** 428 (1909).
[7] Z. Ver. deut. Zucker-Ind. **63,** pt. 1, 25 (1913); Int. Sugar J. **15,** 7, (1913); Am. Sugar Ind. p. 62 (Nov. 1912).
[8] F. J. Bates and R. F. Jackson, Bul. BS **13,** 68 (1916) S268.
[9] Int. Sugar J. **35,** 17, 62 (1933).
[10] Int. Sugar J. **39** (Jan. Suppl. 1937).

XXXVIII APPENDIX 3.—UNITED STATES CUSTOMS REGULATIONS

1. REGULATIONS GOVERNING THE WEIGHING, TARING, SAMPLING, CLASSIFICATION, AND POLARIZATION OF IMPORTED SUGARS AND MOLASSES

[Reprinted from the Customs Regulations of 1937]

The following regulations promulgated by the United States Treasury Department are reproduced here because of their general interest. They were prepared with the cooperation of the National Bureau of Standards.

GENERAL INSTRUCTIONS

Art. 693. *Duties of customs officers (T. D. 46513).*—(*a*) *Duties of entry clerks.*—Estimated duties shall be taken on the entry of Cuban raw sugar on the basis of not less than 96° polariscopic test unless the invoice shows the sugar is of a lower grade than that of the ordinary commercial shipment.

(*b*) All customs officers and employees having duties to perform in connection with the treatment of imported sugars, sirups, and molasses are hereby instructed to use the utmost care and vigilance to insure that the work of weighing, gauging, sampling, classifying, and testing is accurately and efficiently performed.

(*c*) Each inspector, weighing officer, gauging officer, and sampler shall be furnished with a copy of the regulations relative to sugars, sirups, and molasses. The appraiser shall notify the collector of the boundaries of sugar districts and the location of the examiner's or sampler's office in each district, and such information shall be furnished by the collector to the inspectors and weighing officers. The examiners and samplers in charge shall be held responsible by the appraiser for the strict and impartial enforcement of these regulations, and to this end they shall be notified relative to the time of discharge and weighing of sugar and molasses cargoes in their respective districts by the inspector or weigher in charge of the same.

(*d*) *Duties of inspector.*—Inspectors are directed to exercise a personal supervision over the discharging of sugar cargoes. They shall have their permits endorsed by the examiner or sampler in charge after the samples have been obtained in accordance with these regulations. Dock sweepings shall be gathered up and weighed and sampled when discharging has stopped for any cause. The inspector is directed to keep, in every instance, an accurate account of the kind and number of packages of sweepings, which he shall endorse on the back of the permit or lighter manifest before it is presented to the appraiser's office for endorsement. If no sweepings are found, the inspector shall endorse the permit or manifest accordingly.

(*e*) *Duties of weighing officers.*—The weighers shall do the actual weighing and recording of the results, and shall not permit any other person to handle the scales. They shall be required to exercise a strict scrutiny of the conditions under which the weighing is being done, shall keep the scales clean of all foreign accretion, to the end that atmospheric and other exterior influence inimical to accuracy may be avoided, and to obviate the possibility of any drafts passing over the scales unweighed or being reweighed. Scales with beam indicating 1 pound are to be employed in weighing sugar wherever possible.

Art. 694. *Separation of shipments.*—When an importation is consigned to two or more consignees, each consignee's merchandise shall be treated as a separate importation, provided separate entry is made therefor.

Art. 695. *Time of weighing and sampling.*—All sugars and sugar products requiring either weighing or sampling shall have those operations performed at the time of unlading. Merchandise requiring both weighing and sampling shall have those operations performed simultaneously whether discharged under either a regular or a special permit.

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Art. 696. *Absorption of sea water.*—Inasmuch as the absorption of sea water or moisture reduces the polariscopic test of sugar, there shall be no allowance on account of increased weight of sugar importations due to unusual absorption of sea water or of moisture while on the voyage of importation. That portion of the cargo claimed by the importer to have absorbed sea water or moisture on the voyage of importation shall be weighed, sampled, classified, and tested separately. This claim must be made at the time of weighing. Special care must be taken that such sugars are sampled so as to represent the contents of the packages.

Art. 697. *Molasses not for extraction of sugar or for human consumption.* (*T. D. 48127.*)—(*a*) Tariff Act of 1930, paragraph 502:

* * * Molasses not imported to be commercially used for the extraction of sugar or for human consumption, three one-hundredths of 1 cent per pound of total sugars.

(*b*) Such molasses may be released upon the deposit of estimated duties at the rate specified above upon compliance with the following conditions:

(1) There shall be filed in connection with the entry an affidavit of the importer that the molasses is not to be used commercially for the extraction of sugar or for human consumption. For the purpose of these regulations, the phrase "molasses not imported to be commercially used for the extraction of sugar or for human consumption" shall be construed to include, in addition to molasses used in animal feed and other products not for human consumption, molasses which after importation is utilized in the production of articles such as yeast, vinegar, alcohol, rum, gin, or whisky, in such manner that fermentation or other chemical change alters its character and chemical composition so that molasses or sugar does not appear in the final product, and to exclude molasses used for the extraction of sugar, or used either in its condition as imported or after undergoing purifying or blending processes, or both, for table purposes or as a sweetening, coloring, or flavoring agent in the production of articles for human consumption.

(2) If the molasses is entered for consumption there shall also be filed in connection with the entry a bond on customs form 7551 or 7553, with an added condition for the payment of the increased duty in the event the molasses is used contrary to the statements made in the above-mentioned affidavit. Liquidation of the entry shall be suspended pending proof of use or other disposition of the merchandise.

(3) If the molasses is entered for warehouse the regular warehouse entry bond, customs form 7555, shall be given and withdrawals shall be made on customs form 7506. Estimated duty at the rate specified above shall be deposited at the time of withdrawal and the liquidation of the warehouse entry shall be suspended pending proof of use or other disposition of the merchandise.

(4) Within 3 years from the date of entry (in the case of warehouse entries as well as consumption entries) the importer shall submit an affidavit of the superintendent or manager of the manufacturing plant stating the use to which the molasses has been put. If the collector is satisfied that the molasses has not been used in a manufacturing plant but was sold as molasses to the ultimate user, he may accept as proof of the nature of such use an affidavit of the wholesaler or other person making the final sale of the product. Such affidavit shall state the quantity sold and the purpose for which the seller understood the purchase to be made. All affidavits as to use provided for in this subparagraph should state affirmatively the particular use, but may be accepted as sufficient if they specify alternative uses, provided each of the uses so specified is a use other than for human consumption or for the extraction of sugar as defined in subparagraph (1). If the molasses has not been used in the United States, evidence of exportation or destruction satisfactory to the collector should be required. Affidavits as to use and affidavits or other documents showing exportation or destruction should, if practicable, be filed in duplicate, one copy to be forwarded to the comptroller of customs.

(5) Upon satisfactory proof of use of the molasses for purposes other than for the extraction of sugar or for human consumption or of the exportation or destruction thereof the entry may be liquidated at the rate of three one-hundredths of 1 cent per pound of total sugars. When such proof of use or other disposition of the molasses is not made within 3 years from the date of the entry, or the use shown does not warrant the classification claimed, the entry shall be liquidated at the higher rate applicable under the first clause of paragraph 502.

(6) Entries covering blackstrap molasses, as hereinafter defined, may be accepted and liquidated with duty at the rate of three one-hundredths of 1 cent per pound of total sugars after the filing of the affidavit prescribed in subparagraph (1) without compliance with the special requirements of subparagraphs (2), (3),

(4), or (5). For the purposes of these regulations, blackstrap molasses is defined as "final" molasses practically free from sugar crystals, containing not over 58 percent of total sugars and having a ratio of—

$$\frac{\text{total sugars} \times 100}{\text{Brix}}$$

not in excess of 71. In the event of doubt, an ash determination may be made; an ash content of not less than 7 percent indicates a blackstrap molasses within the meaning of these regulations.

(7) The rates of duty above specified are subject to a rebate of 20 percent provided for articles the growth, produce, or manufacture of Cuba, upon compliance with the provisions of article 846.

Art. 698. *Filing of affidavit for molasses in tank cars.*—When an importation of molasses is shipped in tank cars the importer shall file with the collector an affidavit showing whether there is any essential difference either in total sugars or character of the molasses in the different cars. A composite sample shall be made by the examiner to represent the importation. When, in the opinion of the appraiser, the molasses in any of the cars is not identical with that in the other cars, such cars shall be gauged, sampled, classified, and tested separetely.

Art. 699. *Expense of unlading.*—No expense incidental to the unlading, transporting, sorting, or arranging of sugars and molasses for the convenient weighing, gauging, measuring, sampling, or marking thereof shall be borne by the Government. When weighing, gauging, sampling, or measuring is performed concurrently with the unlading, or while the merchandise is being transported from the vessel's side to the importer's premises, no part of the expense of the transportation or handling of the merchandise shall be borne by the Government.

Art. 700. *Standardization of weights and measures.*—In the carrying out of these regulations, all weights and measures shall fully comply with the standards established for such weights and measures by the National Bureau of Standards.

Art. 701. *Mixing classes of sugar.*—No regulations relative to the weighing, taring, sampling, classifying, and testing of imported sugars shall be so construed as to permit of mixing together sugars of different classes, such as centrifugal, beet, molasses, or any sugar different in character from those mentioned, for the purpose of weighing, taring, sampling, classifying, or testing.

WEIGHING OF SUGAR

Art. 702. *Method of weighing.*—All imported raw sugars shall be weighed without regard to mark. Raw sugars are to be weighed gross and, whenever practicable, in drafts of uniform size or of a uniform number of bags, and the tare of trucks and slings, if weighed, deducted periodically as hereinafter prescribed.

Art. 703. *Recording weights—Reports.*—(*a*) The weigher's return shall show the total weight of the cargo, and shall also show separately for each scale, each half day, the weight of all (1) wet sugar, (2) damaged sugar not wet, (3) ship sweepings, (4) dock sweepings, (5) other sugar. The weigher shall make a daily report on customs Form 5993 to the examiner or sampler in charge, which shall show separately for each scale, each half day, the total number of packages weighed of (1) wet sugar, (2) damaged sugar not wet, (3) ship sweepings, (4) dock sweepings, (5) other sugar. All ship and dock sweepings and sugar samples taken before weighing shall be weighed before the weigher completes his half day's work. In no instance shall the weigher make a return by filling in the weight from the invoice.

(*b*) For the purpose of recording and computing net weights, each working day will be divided into four periods, and the weights for each period kept separate, and recapitulated or summarized by starting a new page for each period. All weights are to be recorded in a dock book (or on adding-machine sheets if the latter are used) in the usual manner, the truck number, number of bags in each load, and gross weight being entered in one line. Actual tare of the trucks and slings, if weighed, shall be taken before commencing work in each period by weighing all trucks and all slings for each scale morning and noon and one-half the trucks and slings for each scale for the intermediate periods. The truck numbers, individual and average weight per truck, and total and average weight per sling are to be placed in the middle bottom column, right-hand side of dock book, or in designated place on adding-machine sheets. The total tare, computed according to the number of drafts weighed, shall be deducted from the summary of the gross weight for each period. In computing such tare for each period's work, if a fraction of one-half pound or less results it shall be discarded; if over one-half pound, the next higher unit shall be taken. In addition to the recapitulation, each page must

have denoted thereon the designating scale letter or number, date, and signature of weigher.

Art. 704. *Testing weighing implements.*—Weighers will be required to test and balance their scales or weighmaster's beams with United States standard test weights immediately before the beginning of work and every hour, on the hour, thereafter, and to record the result of balance. They will furthermore be required to see that all trucks and slings used in connection with weighing are maintained at an established uniform weight.

Art. 705. *Automatic scales.*—Wherever available, the Treasury Department automatic scales shall be used in preference to all other types of scales. They shall be under the direct supervision of the mechanical and electrical engineer in charge of scales and that official shall be held responsible for their proper operation and repair. The weigher shall operate the scales in strict accordance with instructions furnished by said official. A copy of these instructions shall be kept permanently in each scale house. All defects in operation shall be promptly reported to said official and a notation in reference to the same made in the dock book or on the adding-machine sheet.

Art. 706. *Custody of scale keys.*—The inspector or officer in charge of the station shall have charge of the keys necessary for the operation of the automatic scales. In commencing the weighing of a cargo it shall be his duty to unlock the scale houses and assign to each weigher or officer acting in that capacity the adjusting and operating keys corresponding to the designating letter of the respective scale, and to the weigher or inspector in charge one scale house key. The station inspector, or where none is assigned, the weighing officer in charge, shall retain in his custody the keys for the record compartment, and under no circumstances permit them to pass into the possession of any other person without written instructions from the collector. At the completion of the day's work it shall be the duty of the inspector in charge to see that the scale houses are locked and otherwise secured against intrusion, and that all electric power is properly switched off. Those to whom keys have been assigned will be held to a strict accountability for their safekeeping.

Art. 707. *Reports on operation of automatic scales.*—At the end of each working day, each weigher (or official acting in that capacity) shall mail to the mechanical and electrical engineer in charge of scales a time slip (customs Form 6031) stating, with the designating letter of scale, the number of hours the scale was in use, the hourly balance weights and adjustments, and the number of bags weighed on the scale in each period, together with the name of the vessel from which the cargo was discharged and a note of any defect in operation of the scales.

Art. 708. *Removal of tapes.*—Upon the completion of weighing of a cargo on an automatic scale, the designated inspector shall remove the printed tape record from the scales. He shall record on the same, legibly and permanently, name of vessel, date of arrival, designating letter of scale, and time of removal of tape; and will be held accountable for the same until properly filed with the weigher's return. Under no condition will the regularly designated inspector permit the keys for the record compartment of the scales to pass into possession of any person not designated by the collector to remove record tapes.

TARING OF CONTAINERS

Art. 709. *Taring by mark (T. Ds. 32796, 37572).*—(*a*) All tare shall be taken by mark. When sugar is in tierces, hogsheads, barrels, boxes, or irregular packages, actual tare shall be taken. When sugar is in bags (other than the standard Cuban sugar bag), baskets, and mats, the actual tare shall be taken and determined by cleaning the following percentage of the receptacles in each mark:

	Percent
Marks of less than 1,000	4
Marks of 1,000 and less than 4,000 (but in no such mark less than 40 receptacles)	3
Marks of 4,000 and less than 10,000 (but in no such mark less than 120 receptacles)	2.5
Marks of 10,000 and over (but in no such mark less than 250 receptacles)	1-2

(*b*) When sugar in the containers mentioned above is discharged and weighed at points other than refineries, actual tare shall be taken of the largest number of receptacles practicable and the percentage tare per mark shall be as nearly as possible that given above.

(*c*) When, in the opinion of the weigher, the condition of the receptacles is such as to make advisable the taring of a larger percentage than that provided above, he shall tare as many receptacles as, in his judgment, are necessary to secure a proper tare. All such receptacles are to be thoroughly cleaned by scraping and sweeping before the tare is taken.

Art. 710. *Schedule tare* (*T. Ds. 33701, 36305, 36306*).—(*a*) In general, there shall be allowed a schedule tare of 2½ pounds per bag for Cuban sugar imported in standard bags. A sugar bag having an area of 1,392 square inches when laid flat (29 inches in width by 48 inches in length) is hereby defined for tare purposes as the standard Cuban sugar bag. When the area of sugar bags varies by more than 2 percent from the standard area of 1,392 square inches, or the bag is not of the usual textile, the schedule tare shall be increased or diminished in proportion to the amount the area or the weight of the bags varies from that of the standard bag. In determining schedule tare, the percentage of the number of bags to be measured for each mark shall be the same as that for actual tare. Where the bags bearing any mark differ in size, the schedule tare allowed shall be based upon the average dimensions of the entire number of bags bearing such mark.

(*b*) In measuring the bags they shall be flattened out to their fullest extent and the folded part at the mouth of the bag shall be turned out. In determining the length, the measurement shall be taken along the seam at the side. In determining the width, the measurement shall be taken across the back at a distance of about 4 inches from the mouth.

Art. 711. *Actual tare* (*T. Ds. 36305, 36306*).—In determining actual tare, all bags shall be selected with careful discrimination as to condition and every care exercised to insure their accurately representing the mark. The bags shall be carefully dry-cleaned by sweeping and scraping and then weighed, which weight shall be taken as the actual tare.

Art. 712. *Verification of schedule tare* (*T. D. 32976*).—When the collector has reason to doubt the correctness of any schedule tare, he shall verify such schedule tare by taking actual tare. If the importer shall file a written application representing that there is an excessive number of damaged bags in a given importation and shall give the approximate percentage of the damaged and sound bags, and shall on that account request that actual tare be taken, the collector, if satisfied that the facts are as stated, shall determine the actual tare on the importation.

Art. 713. *Acceptance of actual tare.*—Whenever actual tare is determined on any importation and is found to differ from the schedule tare by not more than 5 percent, the schedule tare shall be allowed on such importation. In the event that the actual tare differs from the schedule tare by more than 5 percent, the actual tare shall be the accepted tare.

GAUGING OF MOLASSES

Art. 714. *Plans of storage tanks.*—Where molasses is imported in bulk in tank vessels and is to be pumped or discharged into storage tanks, the gallonage capacity of the latter, per inch in height, shall be ascertained while the storage tank is empty on the basis of 231 cubic inches to the gallon. Before the discharging is permitted, there must be on file in the customhouse a certified copy of the plans of the storage tank, showing all inlets and outlets. All outlets of the storage tank shall be sealed by the gauger before pumping begins. In the event a storage tank is partially filled with molasses, the gauger will ascertain the quantity contained therein before the pumping of the new importation is commenced. He shall also carefully examine the pump line to see that the same is in good condition.

Art. 715. *Time of gauging* (*T. D. 42927*).—After the discharge is completed, all inlets to the tank will be carefully sealed and the molasses left undisturbed for a period not to exceed 20 days, to allow for settling, before being gauged. When the importer requests in writing immediate gauging, the same shall be allowed by the collector.

Art. 716. *Tank gauging.*—The report of the gauging of the molasses shall show the number of gallons of molasses and the temperature of the molasses in degree centigrade determined at the time of gauging. Report as to gauge and temperature is to be made to the examiner (customs Form 5991). The depth of the molasses contained in the storage tank shall be ascertained by means of a steel rod, having a movable brass scale expressed in inches and tenths of inches. The measurement shall be taken from the bottom of the tank to the top of the liquid, deduction being made for the molasses, if any, contained in the tank before the discharge began. If there is foam present the gauging shall be made with the aid of the "foam can", which shall be in accordance with the following specifications: The foam can shall be made of heavy galvanized-iron pipe 5 feet long by 7½ inches in diameter fitted at the bottom with a wooden plug attached to the can by means of a chain, and fitted at the top with suitable hooks for attaching ropes for lowering. The method of using shall be to place the wooden plug in the bottom of the can and lower the can into the molasses by means of the ropes attached to the top. The gauging rod is passed through the can, releasing the wooden plug at the

bottom, allowing the molasses to flow into the can to the level of the molasses in the tank. The gauging rod is then lowered through the can to the bottom of the tank and an accurate gauge of the molasses without foam is registered on the gauging rod. This procedure shall be followed both on immediate gauging as well as gauging after the lapse of the 20-day period in all cases where foam is present. No allowance shall be made for occluded air or other gases in the body of the molasses. The depth of the imported molasses having been ascertained in inches, the result will be multiplied by the number of gallons per inch in height previously ascertained when the storage tank was measured empty.

Art. 717. *Gauging tank cars.*—When molasses is imported in tank cars the quantity contained therein will be ascertained by gauge.

SAMPLING OF SUGARS, SIRUPS, AND MOLASSES

Art. 718. *General sample defined (T. D. 33228).*—(*a*) In sampling imported raw sugars, a general sample shall be taken, that is, each importation shall be sampled without regard to marks and 100 percent of the packages shall be sampled. A separate general sample shall also be taken of (1) wet sugar, (2) damaged sugar not wet, (3) ship sweepings, (4) dock sweepings. In order to prevent any unnecessary labor and inconvenience in obtaining the sample, the inspector shall direct that the packages when discharged from the vessel upon the wharf shall be so placed that the sampler can readily obtain a 100-percent sample. All ship and dock sweepings shall be sampled before the sampler completes his half day's work. It shall be the duty of all samplers to secure a thoroughly representative sample.

(*b*) In sampling separate importations of sirups or molasses placed in the same tank, care must be taken to get truly representative samples of each lot.

Art. 719. *Stained bags (T. D. 33228).*—In the event that bags are stained from lying in storage, or from any other cause, but the sugar not damaged, the sampler in charge, as well as all other samplers, shall exercise every precaution to see that the bags come alternately with the clean and stained sides up. When, in the opinion of the sampler in charge, the bags are not being so discharged, he shall direct the attention of the inspector to that fact, and it shall be the duty of the inspector to thereupon stop the discharge of the cargo until the instructions of the sampler are complied with. If, from any cause, in any cargo, the condition of the bags from the ground tier or any other tier shall differ markedly from the condition of the cargo as a whole, such bags shall be treated as damaged.

Art. 720. *Care of samples—Letter of transmittal—Keys.*—(*a*) In the treatment of sugars under these regulations, great care shall be exercised by samplers and other appraising officers to prevent the drying out of samples, as well as their absorbing moisture. A standard sugar bucket shall be used in which to collect the samples. It shall be made of heavy galvanized iron and have a height of 31½ centimeters and a diameter of 18½ centimeters. The covers of the buckets must be kept closed, except when momentarily opened to receive the sample. All the buckets containing samples from a given half day for each cargo shall be filled, with the exception of one. The label on each bucket must identify the sugar and the particular half day on which its contents were drawn and the name of the officer responsible for the sampling of same. All buckets, after being so labeled, shall be locked before leaving the spot where the samples are being drawn. The examiner or sampler in charge shall forward the samples to the appraiser's stores with a dock list on customs Form 6483-B, on which partially filled buckets shall be noted as one-fourth, one-half, or three-fourths. After the discharge of the cargo has been completed the examiner or sampler in charge shall forward a letter of transmittal to the appraiser on customs Form 6461.

(*b*) The keys of the locks used on sugar buckets shall be in possession of the assistant appraiser or the examiner at the appraiser's office, who shall have sole custody of such keys.

Art. 721. *Dimensions of sugar triers.*—The sugar triers used shall have the following dimensions:

	Short trier	Long trier	Barrel trier
	Centimeters	*Centimeters*	*Centimeters*
Length over all	40.6	152.4	104.0
Length to spoon	22.9	132.1	91.4
Length of shank	17.8	20.3	12.7
Length of handle	26.7	38.1	30.5
Width of spoon	2.7	2.5	2.5
Depth of spoon	.8	1.3	1.1
Diameter of handle	3.8	3.8	3.8

Art. 722. *Receptacles—How sampled.*—Sugar in hogsheads and other wooden packages shall be sampled by putting the long trier diagonally through the package from chime to chime, one trierful to constitute a sample, except in small lots, when an equal number of trierfuls shall be taken from each package to furnish the required amount of sugar necessary to make a sufficient sample. In the sampling of baskets, bags, seroons, and mats the short trier shall be used, care being exercised to have each sample represent the contents of the package. The greatest precaution shall be taken that the samples from each class of packages shall be kept separate and be uniform in quantity.

Art. 723. *Detail of samplers.*—At ports where the number of samplers employed will permit, no sampler shall be detailed in the same sugar district or on the same dock longer than one month. A complete record of the assignment of the examiners and samplers shall be kept and shall be approved by the appraiser.

Art. 724. *Discharge from lighters.*—Sugars conveyed on lighters from the place of original discharge before samples have been taken shall not be removed therefrom until notice of the time of their proposed removal has been given by the inspector to the examiner or sampler in charge.

Art. 725. *Sampling from lighters.*—In cases where vessels discharge in one district and the sugars are lightered to another before sampling, the manifest which accompanied the lighter and is delivered to the inspector in charge of the district where such sugars are to be weighed and sampled shall be presented to the examiner or sampler in charge for his indorsement, the same as in the case of an original permit and such manifest shall show the name of the person making entry. The inspector in charge of such district shall be held responsible for the treatment of all such sugars under these regulations, the same as if working under the original permit.

Art. 726. *Transfer of samples.*—All sugar samples drawn on any given half day shall reach the examining room in the appraiser's stores not later than the close of the first official half day following, except where the place of discharge is more than 15 miles distant from the appraiser's stores. Whenever practicable the samples for each half day will be forwarded to the appraiser's stores as soon as the half day is completed. When sugars are discharged at places where the distance makes it impracticable for the regular conveyance to call for the samples, and where special provision is made by contract for other means of transportation, an official shall be detailed by the appraiser to take charge of such sample until they reach the appraiser's stores.

Art. 727. *Refined sugars.*—In sampling receptacles containing refined sugars the percentage to be sampled shall be determined by the best judgment of the examiner or sampler in charge. Every precaution shall be taken to have the sample fairly and adequately represent the shipment.

Art. 728. *Care of sampling equipment.*—The utmost care must be taken to keep all the apparatus used in the process of sampling sugar clean and absolutely dry. Suitable cleaning and polishing materials shall be supplied to the samplers, who are hereby instructed to always have their implements in perfect condition. The sampler shall frequently and thoroughly clean his trier with a scraper provided for that purpose. Failure to observe these requirements shall be reported at once to the appraiser by the examiner or the sampler in charge, and such failure will be regarded as sufficient cause for suspension.

Art. 729. *Sugar discharged during storm.*—Sugar discharged during a rain or snow storm shall be sampled under cover. When this is impracticable, or if in the judgment of the appraiser fair samples cannot be obtained by reason of the stress of weather, or for any other reason, the inspector shall immediately stop the discharge of the cargo. In the absence of the inspector the appraiser shall immediately take such steps as may be necessary to stop the discharge of the cargo.

Art. 730. *Buckets for sirup and molasses samples.*—The receptacle used in collecting all molasses samples shall be the standard sugar bucket, and the regulations governing the use of this bucket in the collection of sugar shall apply with equal force when it is used for the collection of molasses.

Art. 731. *Molasses and sirups—Better grades (T. D. 36195).*—In sampling all grades of sirups and molasses other than blackstrap, 100 percent of the packages shall be sampled. The contents of each receptacle shall be thoroughly stirred in order that any settlings shall be evenly distributed and the contents brought to as uniform a density as possible. Receptacles of the same size shall be sampled in groups of not more than 25, a sample of uniform quantity being drawn from each. A tally shall be kept and the label thereon shall show the number of packages which each bucket represents. The dock list accompanying the sample buckets shall convey the same information and shall account for every package of the

mark. Packages of different size or character of contents, although invoiced and permitted under the same mark, shall be separately sampled, tested, and classified. If any package or packages shall, in the judgment of the sampling officer, have the appearance of sirup of cane juice, or of testing by the polariscope above 50 sugar degrees, a separate sample of same shall be taken.

Art. 732. *Blackstrap molasses.*—When blackstrap (frequently designated waste molasses) is imported in barrels, 10 percent of all the receptacles shall be sampled. When, in the judgment of the examiner or sampler in charge, a greater percentage is necessary to fairly represent the importation, such additional barrels shall be sampled as, in his judgment, are necessary to secure a representative sample. Blackstrap imported in tank vessels shall be sampled as it is being pumped from the vessel. Samples of uniform quantity, in general one-half liter, shall be drawn with such frequency as to insure one sample for each 5,000 gallons.

Art. 733. *Molasses in tank cars.*—Molasses in tank cars shall be sampled by drawing two similar complete samples of about 1 liter each and consisting of a continuous portion or core extending from the top to the bottom of the tank. When for any reason such a core cannot be obtained, the two complete samples shall each consist of three portions: One portion from the top just below the surface of the liquid, one from the center, and one from the bottom of the tank. All samples shall be forwarded to the appraiser with the least possible delay.

Art. 734. *Sugar closets.*—Sugar closets in the sugar districts shall be substantially built, and secured by locks furnished by the Department. They shall be conveniently located as near as possible to the points of discharge they are intended to serve. They shall be provided by the owner of the premises on which they are located and shall be so situated that sugar, sirup, and molasses stored therein shall not be subjected to extremes of temperature or humidity.

TESTING OF SUGARS, SIRUPS, AND MOLASSES

Art. 735. *Mixing of sugar samples.*—The mixing and preparing of samples for test shall be done at the appraiser's stores under the supervision of the examiner of sugar. Samples shall be mixed and forwarded to the laboratory as soon as possible after their arrival at the appraiser's stores. Under no circumstances shall the contents of more than three sugar buckets be mixed together. The mixing shall be performed on heavy paper with a glossy surface which will not readily absorb moisture, or on a table with a metal top. The samples shall be passed through a wire screen of about $^{3}/_{8}$-inch mesh set in a galvanized-iron frame with inclosed sides. Great care shall be exercised to obtain a uniform mixture, but the operation shall be expedited so as to avoid unnecessary exposure to the atmosphere.

Art. 736. *Sugar cans.*—The tin cans used in transmitting the samples to the laboratories for polariscopic test shall have a height of 11.5 centimeters and a diameter of 8 centimeters. They shall be practically airtight, the seamless lid fitting snugly over the rim, which is topped by a seamless band. No cans shall be used for this purpose that have not been made on the dies owned by the Department. All cans must be clean and dry before using. Frequent inspection shall be made to prevent the use of any can having loose or ill-fitting lid or broken seams on side or bottom. All damaged cans shall be discarded.

Art. 737. *Preparation of sugar samples.*—From the sample prepared by mixing the contents of not more than three buckets, duplicate samples shall be prepared by closely packing two tin cans full of sugar and transmitted forthwith to the laboratory for polariscopic test. Where the port of importation has no customs laboratory, the prepared samples shall be transmitted forthwith to the chief chemist of the customs laboratory designated in article 12 and the cans of samples shall be firmly packed full of sugar and sealed airtight with paraffin. A third portion, consisting of about three pounds, shall be placed in a glass jar to constitute a reserve sample. In all cases the jars must be firmly packed full of sugar before closing and so sealed as to make them airtight. Such samples, after being properly labeled for identification, shall be held in safe custody by the appraiser for use when required.

Art. 738. *Identification of samples.*—In transmitting the samples from the examiner's room to the laboratory they shall be indicated only by serial numbers, the key to which shall consist of the appraisement lists, on which the same numbers must appear, and the laboratory officers shall not be informed in any manner as to the identity of such samples. Appraisement lists shall be made out in duplicate, an original and carbon copy, the latter to be filed in the order of the sample serial numbers for reference if required. Sample serial numbers shall begin with No. 1 at the beginning of each year and continue throughout the year, and all numbers shall be accounted for in the records specified.

Art. 739. *Recording of sugar tests.*—A complete test shall be made of each sample sent to the laboratory. The accepted tests reported by the chemist in charge shall be entered in red ink on the original appraisement lists, together with the accepted tests of the duplicate samples. Should the accepted tests of duplicate samples provided for in article 738 be 92° S (sugar degrees) or above and should they agree within 0.2° S, the average of the two shall be taken as the true polariscopic test of the sugar. If one or both of the polarizations should be less than 92° S, and they agree within 0.3° S, the average of the two shall be taken as the true polariscopic test of the sugar.

Art. 740. *Use of reserve sugar sample.*—When the accepted tests of the two samples do not agree as provided in article 739, a third sample, to be known as the reserve sample, shall be made up from the reserve portion, and treated as a regular sample. When preparing samples for the laboratory from the reserve jars the entire contents shall be taken out and remixed in order that the moisture may again be evenly distributed throughout the sample. The tests of the reserve sample having been duly recorded, the accepted tests of the three samples shall be considered together. Of the three separate tests so recorded, the average of the two most closely corresponding shall be taken as the test of the sugar; but if one of the said tests be the average of the other two it shall be taken as the correct test.

Art. 741. *Sugar test for classification.*—(*a*) The test for classification shall be an average of tests based upon the number of packages which each accepted test represents. This number shall be determined by proportioning the number of packages weighed each half day over the different mixings for such half day according to the number of cans of samples received, using the reports of the weigher, provided for in article 703, for that purpose. Such average shall be carried to five places of decimals.

(*b*) Wet sugar, damaged sugar not wet, ship sweepings, dock sweepings, or any other sugar required under these regulations to be sampled separately, shall be classified and the tests averaged in the same manner as the general cargo.

Art. 742. *Retests of sugar.*—(*a*) When the test of the sugar has been determined the appraiser shall immediately notify the importer of the average test of the importation and also the quantity and test of each lot from which such average test is obtained. Should be importer, within 2 official days after such notice has been sent to him by the appraiser, claim an error in the test so reported and request a retest, such retest may be granted, provided, on evidence furnished, such claim shall appear to the appraiser to be well founded. Before granting retest the appraiser shall require of the importer any information he may deem desirable relative to the samples and polarizations used in the settlement tests. Before any sugar invoice is passed the appraiser shall require the importer to furnish the settlement tests, and in no instance shall a retest be granted when the difference between the appraiser's test and the settlement test is shown to be less than 0.4° S. Samples for retest shall be made up from the reserve sample and shall be treated in all respects as provided for the original tests.

(*b*) All requests for retests of sugar shall be properly filed and a record thereof shall be kept by the appraiser on customs form 6467.

Art. 743. *Classification when retest is made.*—In case of retest made under the provisions of article 742, the test upon which the sugar shall be classified shall be the average of the test and the retest unless it can be shown to the satisfaction of the appraiser that either the test or the retest is in error, in which event the test not in error shall be taken as the basis of classification.

Art. 744. *Error in original test.*—In all cases where in the judgment of the appraiser an error has been made the reserve sample may be resorted to by the appraiser at any time before he has made his return on the invoice for the purpose of determining and correcting such error.

Art. 745. *Molasses and sirup samples—Preparation and recording of tests* (*T. Ds. 31762, 31935*).—(*a*) All the molasses and sirup samples from an individual importation, when uniform in character, shall in general be represented by not more than two composite laboratory samples each sample representing one-half of the importation. Whenever practicable, a single composite sample shall be made to represent the importation. When, however, any such samples are not uniform in character, or when separate samples have been returned pursuant to article 732, as many separate samples shall be sent to the laboratory for test as, in the judgment of the examiner, shall be necessary to correctly classify the different grades of material in the importation.

(*b*) Two duplicate samples of approximately one-half liter from each composite sample shall be forwarded with the least possible delay to the laboratory for test.

At least 1 liter of each composite sample shall be retained as a reserve sample. The average of the tests of the duplicate samples shall be the accepted test of the composite sample provided they do not differ by more than five-tenths percent total sugars.

(*c*) The contents of each bucket of molasses or sirup samples shall be stirred in such a manner as to evenly distribute any sugar sediment that may have settled to the bottom and the contents brought to as even a density as possible.

(*d*) The recording and averaging of accepted tests of duplicate samples shall be, unless otherwise provided for in these regulations, the same as for sugar. Molasses and sirup samples shall be labeled with customs form 6479 showing the following information: Invoice designation; entry number; marks; place and date of sampling, sampler; entered paragraph and rate; origin; also, when shown on the customs invoice, the percentage by weight of total soluble solids (or Brix) and the percentage by weight of total sugars.

(*f*) Molasses and sirup samples shall be handled as expeditiously as possible in order that they may not be affected by fermentation and shall be given a serial number that will insure as early a test as possible.

Art. 746. *Molasses and sirup test for classification.*—The test for classification of a molasses or sirup importation shall be the average of the accepted tests for the composite samples based upon the proportion of the entire lot which each composite sample represents.

Art. 747. *Molasses and sirup—Significance of test—Retest (T. D. 39710).*—Owing to the unstable character of molasses and sirup, the results of any retest cannot have, from the standpoint of correctness for appraisement purposes, the same significance which the results of a retest on sugar possess. A retest shall be granted by the appraiser only when the information in his possession indicates a strong probability of an error. The regulation governing the granting of a retest shall in general be that given in article 743, with the exception that the difference between the appraiser's test and the settlement test shall be shown to be not less than 2 percent total sugars.

Art. 748. *Notice to importer.*—When an invoice of sugar, molasses or sirup has been passed, the appraiser shall at once send written notice to the importer, informing him of the test for classification of his importation.

Art. 749. *Sugar records—Filing.*—The original appraisement lists for each cargo, with dock lists, weighers' reports, letters of transmittal, and any other information relating to the same, shall be filed together as a permanent record, under serial numbers, an index to which shall be kept in a permanent form as a means of ready reference. All chemists' reports of tests shall be filed in the order of the sample serial numbers for reference when required.

Art. 750. *Procedure for exchange samples.*—(*a*) Each day, except as provided for in paragraph (*b*), when imported sugar is sampled for test at any port, the appraiser shall prepare a duplicate of one of the regular laboratory samples referred to in article 737 and forward the duplicate to the Director of the National Bureau of Standards. The sample sent to the customs laboratory shall be tested as soon as it is received and the separate tests, together with the accepted test, shall be immediately reported, under the identifying marks by the appraiser at the port where the samples were mixed for testing, to the Director of the National Bureau of Standards on customs form 6473. The report on customs form 6473 for all ports shall show the polarization. On Firdays at each of the ports of Baltimore, Boston, New Orleans, New York, Philadelphia, Savannah, San Francisco, Los Angeles, and Chicago, the exchange sample sent to the customs laboratory and the duplicate sent to the National Bureau of Standards shall each be designated "dry", and the report on form 6473 shall show, in addition to the polarization, the percent of moisture and the polarization of the dry substance.

(*b*) On Monday of each week each appraiser at Baltimore, Boston, New Orleans, New York, Philadelphia, and Savannah shall prepare a sample of sugar for test in the customs laboratory at his port, and a duplicate of the same sample shall be forwarded to each of the other appraisers at the above-named ports and to the Director of the National Bureau of Standards. Upon receipt of a duplicate exchange sample at a port, it shall be entered in a special record, after which the identifying marks shall be carefully removed and the sample delivered to the customs laboratory under its serial number. The sample shall be tested as soon as it is received and the separate tests, together with the accepted test, shall be immediately reported by the appraiser under the identifying marks to the Director of the National Bureau of Standards on customs form 6473. A copy of this report shall be forwarded at the same time to the Commissioner of Customs. The report on customs form 6473 shall show the polarization.

(*c*) Each sample shall be forwarded in the tin can prescribed in article 736, which shall be firmly packed full of sugar and sealed airtight with paraffin. The samples shall be numbered at each port of importation from 1 upward, beginning with the first official day in each calendar year, and the duplicates shall be marked for identification with the same number, the name of the importing port, and the date of the test at such port. A complete record of sample tests shall be kept on customs form 6481.

(*d*) All requests by the Director of the National Bureau of Standards (Department of Commerce form 558) for retests of the polarization or of the polarization of the dry substance of samples shall be immediately complied with. The retests shall be completed not later than the close of the first official day after the receipt of the request, and the results immediately forwarded by the appraiser on customs form 6473. When, for any reason, the retests requested are not completed by the close of the first official day after the receipt of the request, the retests shall not be made and the appraiser shall furnish the Commissioner of Customs with a detailed statement why said retests were not made as herein provided.

Art. 751. *Molasses and sirup exchange samples.*—Once each month, when imported molasses or sirups are sampled for test at any port, the appraiser shall prepare a duplicate of a sample sent to the customs laboratory designated in article 12 and forward the duplicate half-liter sample, properly numbered and labeled, to the Director of the National Bureau of Standards for test. A copy of the customs laboratory report, customs form 6415, shall be promptly forwarded to the Director of the National Bureau of Standards by the appraiser of the port where the molasses was mixed for transmission to the laboratory. The report shall show separately the percent sucrose, the percent reducing sugars, the percent total sugars, the percent nonsugar solids in total soluble solids, and the weight per gallon in air at 20° C. The samples shall be numbered at each port of importation from 1 upward, beginning with January 1 of each year, and the duplicates shall be marked for identification with the same number, the name of the importing port, and the date on which the sample was prepared. The samples shall be transmitted in screw-top metal containers. A reserve portion of each such sample, consisting of not less than one-half liter, shall be retained by the appraiser for retest purposes. All requests by the Director of the National Bureau of Standards for retests shall be promptly complied with.

Art. 755. *Adulterated refined sugars.*—When refined sugars, including all sugars other than raw sugars, are imported at any port, samples shall be forwarded to the customs laboratory designated in article 12 to determine whether, after having been refined, they were tinctured, colored, or in any way adulterated. A duplicate of each such sample sent to the customs laboratory shall be forwarded at the same time to the National Bureau of Standards. Each sample sent to the customs laboratory and each duplicate sent to the National Bureau of Standards shall be placed in the sugar can described in article 736 and labeled with customs form 6479. The cans shall be firmly packed full of sugar and sealed airtight with paraffin. A copy of each customs laboratory report on such samples shall be transmitted to the National Bureau of Standards.

Art. 756. *Preservation of sugar samples.*—All samples of sugar sent to the laboratory for test must be preserved as nearly as possible in the same condition as when received, and shall be returned therefrom to the examining room in such condition. All samples tested for exchange and all exchange samples, as soon as they have been returned from the laboratory, shall be labeled with their identifying marks, securely sealed airtight, and held in safe custody in the examining room 30 days from the date of test for such further test or investigation as may be ordered by the Director of the Bureau of Standards. In case any exchange samples have been received at any port not properly filled and sealed as herein prescribed, the appraiser at the port of receipt shall immediately notify the appraiser at the port of transmittal, and shall also report the facts to the Director of the Bureau of Standards.

Art. 757. *Care of apparatus.*—All screens used in the mixing of samples, sample buckets, sample cans, reserve jars, etc., when once used, shall be thoroughly washed, dried, and allowed to cool before being used a second time.

Art. 758. *Admission to examining rooms.*—All persons shall be denied admission to the examining rooms of the appraiser's office except officers and employees whose duties require them to have access thereto. This provision must be strictly enforced.

Art. 759. *Interpretation of "testing by the polariscope."* The expression "testing by the polariscope * * * sugar degrees", occurring in a tariff act, shall be construed to mean the percentage of sucrose contained in the sugar shown by direct polarimetric estimation.

Art. 760. *Total sugars defined.*—The expression "total sugars", occurring in the tariff act, shall be construed to mean the sum of the sucrose (Clerget), the raffinose, and the reducing sugars.

Art. 761. *Laboratory records.*—A permanent record of all samples received from the examiner shall be kept in the laboratory. The samples shall be identified therein by their serial numbers arranged in the order in which they are received. It shall be the duty of the chemist in charge to report the results of all tests of such samples made and recorded, severally, including the third and fourth tests, when made, to the assistant appraiser or examiner in charge of classifications.

LABORATORY PROCEDURE FOR SUGARS, SIRUPS, AND MOLASSES

Reprinted from Customs Regulations of 1931, Articles 741–756, inclusive and Articles 758–763, inclusive

Arrangement of laboratories.—Plans for laboratories for the testing of sugar and molasses must be approved by the Commissioner of Customs. The room used for the purpose shall be one that is as far removed as possible from the vibration of machinery; it must be well lighted and have some means of artificial heat, so that the temperature may be controlled, and shall not be too near any source of heat which cannot be controlled. The polariscopes shall be placed in the darkest portion of the room whenever possible, and the top of the table upon which they are placed shall be surrounded on three sides by blackened partitions or walls not less than 3 feet in height. If necessary, suitable curtains may be hung around the polariscope to exclude extraneous light. The surroundings of the polariscope shall be such as always to permit the air from the remainder of the room to circulate around the instruments with the greatest freedom. The separation of the lamp from the instruments will be accomplished by the wall around the top of the table. The opening in the partition between the lamp and the instrument shall be as small as possible and yet allow sufficient light for the proper illumination of the polariscope. The polariscope shall not be near ovens, assay furnaces, hot-water heaters, or any other source of heat.

Standardized apparatus.—All thermometers, flasks, weights, polariscope tubes, polariscope-tube cover glasses, quartz control plates, and polariscopes, used in the work of testing sugar, shall be standardized at the Bureau of Standards, Department of Commerce, and with the exception of the polariscope-tube cover glasses and weights, shall be marked with the initials "U. S. C. S.", and bear the stamp of the Bureau of Standards. No test of sugar shall be made with apparatus which is not properly marked unless special authority is given by the Secretary of the Treasury.

Standardization temperature.—All the apparatus used in the work of testing sugar by the polariscope shall be standardized at a temperature of 20° C.

Thermometers.—All thermometers shall have the centigrade scale and be graduated to one-fifth of a degree or less.

Sugar flasks.—(*a*) The flasks shall have a height of 130 mm.; the neck shall be 70 mm. in length and have an internal diameter of not less than 11.5 mm and not more than 12.5 mm. The upper end of the neck shall be flared, and the graduation marks shall be not less than 30 mm. from the upper end and 15 mm. from the lower end of the neck.

(*b*) All flasks shall be standardized to contain 100 ml. at 20° C. The glass funnels used in filtering shall have a diameter of approximately 90 mm. The cylinders shall have a height of approximately 125 mm. and a diameter of approximately 40 mm.

Laboratory weights.—Only brass weights shall be used, and they shall be forwarded to the National Bureau of Standards for standardizing not less than once a year. A sufficient number of standardized duplicate weights shall be kept in reserve in each laboratory to take the place of those being standardized.

Polariscope tubes.—The length of all polariscope tubes shall be either 100 ± 0.03 mm. or 200 ± 0.03 mm., and the diameter of the opening through the tube shall be not less than 9 mm. No tube shall be retained in use that has become bent or dented or has had its threads injured sufficiently to make the adjustment of the cap difficult.

Quartz control plates.—All quartz control plates shall be mounted in a brass retaining box, which shall exert no pressure whatever upon the plate and yet allow it minimum play. Each plate will be accompanied by a table, signed by the Director of the Bureau of Standards, giving its exact value at different temperatures from 15° to 35° C.

Standard sugar solution.—All polariscopes shall be so standardized that when a 200-mm. tube filled with the standard sugar solution is polarized at 20° C. the instrument shall read 100° $\pm 0.01°$ S. All points on the scale shall indicate per-

centages of the standard solution. The standard sugar solution shall be prepared by dissolving 26 g. of pure sugar in pure water and making up the volume to 100 ml., all weighings to be made in air with brass weights and the volume to be completed at 20° C. A length of 200 mm. of the standard sugar solution shall be considered to give a rotation of 40.763° for light of wave length 5461×10^{-8} cm.

Polariscopes and their adjustment.—(*a*) All polariscopes used in the testing of imported sugars shall have a double quartz-wedge compensation and a polarizing system known as the Lippich half shadow. The field of the polariscope shall be divided into halves by a vertical line, and in no instance shall a reading of the scale be made unless, in the opinion of the observer, the halves are of exactly equal intensity.

(*b*) If, when the polariscope is empty and the halves of the field matched, the zero of the movable scale shall fail to correspond with the zero of the vernier by more than 0.3° S (sugar degrees), they shall be made to coincide by turning the small nipple on the left-hand side of the instrument.

(*c*) In testing the instrument by means of the quartz control plate, not less than four careful readings shall be made. After the average of these readings has been corrected for the error in the zero point, it should equal the value stamped upon the plate within 0.05° S. If such is not the case the polariscope shall be readjusted until the difference is not greater than 0.05° S.

(*d*) When taking the reading on the quartz control plate the deviation of the zero point shall be neglected after the instrument has been found to be accurately adjusted. The total correction for the instrument shall then be found by means of the table accompanying the plate and the reading of a thermometer placed close to the polariscope.

(*e*) The method of determining and applying the total correction shall be as follows: Let a sugar solution polarize 95.55° S. The control plate had polarized 99.95° S. The temperature of the room during both observations was 25° C. From the table the value of the control plate at 25° C. is 100.25° S. The reading is therefore 0.30 too low and 0.30 shall be added to the reading of the sugar solution, making the corrected polarization 95.85° S.

(*f*) The zeros of the upper scale and its vernier shall be kept in exact coincidence and the scale securely clamped in that position.

Polariscope light source—Bichromate cell.—(*a*) The source of light may be either an incandescent gas mantle or white-light electric lamp constructed according to the specification of the Bureau of Standards. The radiating source shall not be less than 200 mm. distant from the polarizing end, the best position of the source being determined by carefully adjusting it back and forth until the illumination of the field is absolutely uniform and a maximum.

(*b*) The radiation from all white-light sources shall be filtered through a solution of potassium bichromate before it enters the polariscope. This solution shall be contained in a glass cell, placed as near as possible to the polarizing end of the instrument. The cell shall have parallel walls with an inside separation of 15 mm. The concentration of the solution shall be 6 percent. If, for any reason, it should be necessary to use a cell which does not give a layer of liquid 15 mm. thick, the concentration must be so altered that the product of the thickness in millimeters of the absorbing solution and the concentration, in percent, shall equal 90.

Preparation of the sugar solution.—After the can of sugar referred to in article 737 [48] above has reached the laboratory its contents shall be thoroughly mixed while in the can by stirring with a spoon just before the weighing is made. In case the sugar contains hard lumps not readily crushed and mixed by stirring, it shall be mixed in a mortar or by other adequate means. In case of sugar products in liquid form, such as sirup of cane juice and mixtures containing sugar and water, the sample shall be thoroughly mixed to insure uniformity. If sugar crystals have separated out, they must be redissolved by placing the sample in a water bath at approximately 50° C. Care must be exercised to prevent undue evaporation during the heating, mixing, and in the weighing of the sample for analysis. After mixing, 26 g. are weighed on the balance in the tared German-silver dish furnished for this purpose. Care must be taken that the operations of mixing and weighing are not unduly prolonged; otherwise the sample may easily undergo a change in the moisture content. The weighed portion of sugar is washed by means of a jet of water into a 100-ml flask, the dish being well rinsed three or four times and the rinsings added to the contents of the flask. The water used must be either distilled water or clear water, which has been found to have no optical activity. After the dish has been thoroughly rinsed, enough water is added to bring the contents of the flask to about 60 ml., and it is gently rotated

[48] Article 737, Customs Regulations of 1937.

until all the sugar is dissolved. The flask shall be held by the neck and the bulb not handled during this operation. A proper mechanical shaking device may be used in place of hand shaking. Care must be taken that no particle of the sugar or solution is lost. To determine whether all the sugar is dissolved, the flask is held above the level of the eye, in which position any undissolved crystals can be easily seen at the bottom. The character of the solution is now observed. If it be colorless, or of a very light straw color, and not opalescent so that it will give a clear, transparent liquid on filtration through paper, the volume shall be made up directly with water to the 100-ml mark on the flask.

Use of basic lead acetate.—(*a*) If a clear, transparent liquid is not obtained, a clarifying agent shall be added In that event, before making up to the mark a solution of basic acetate of lead is added, which is prepared by boiling 3 parts by weight of acetate of lead, 1 part by weight of oxide of lead, and 10 parts by weight of water until the reaction is complete. The filtered solution should have a density of about 1.25. Solid basic acetate of lead may be substituted for the normal salt and oxide in the preparation of the solution.

(*b*) After adding the solution of basic acetate of lead the flask must be gently shaken, so as to mix it with the water solution. If the proper amount has been added, the precipitate will usually subside rapidly; but if not, the operator may judge of the completeness of the precipitation by holding the flask above the level of the eye and allowing an additional drop of basic acetate of lead to flow down the side of the flask into the solution. If this drop leaves a clear track along the glass through the solution, it indicates that the precipitation is complete. If, on the other hand, all trace of the drop is lost on entering the solution, it indicates that an additional small quantity of the basic acetate of lead is required. The operator must learn by experience the point where the addition should cease; an excess of basic acetate of lead solution should never be used.

Making up to volume and filtering.—(*a*) The solution shall be made up to the mark by the addition of distilled water in the following manner: The flask, grasped by the neck between the thumb and finger, shall be held before the operator in an upright position, so that the mark is at the level of the eye, and water is added, drop by drop, from a siphon bottle or wash bottle until the lowest point of the curve or meniscus formed by the surface of the liquid just touches the mark. If bubbles hinder the operation, they may be broken up by adding a single drop of ether or a spray from an alcohol atomizer before making up to the mark. After making up to volume, drops of water adhering to the neck above the meniscus shall be removed. The mouth of the flask shall be tightly closed with the thumb, and the contents of the flask shall be thoroughly mixed by turning and shaking. The entire solution shall be poured upon the filter.

(*b*) The funnel and the vessel used to receive the filtrate must be perfectly dry. The first portion of the filtrate, about 20 to 30 ml, should be rejected entirely. It may be necessary to return subsequent portions to the filter until the liquid passes through perfectly clear.

(*c*) If a satisfactory clarification has not been obtained, the entire operation must be repeated, since only with solutions that are entirely clear and bright can accurate polarimetric observations be made.

Filling and handling of polariscope tube.—When a sufficient quantity of the clear liquid has passed through the filter the 200-mm polariscope tube shall be filled with it. The 100-mm tube should never be used except in the rare cases when, notwithstanding all the means used to effect the proper decolorization of the solution, it is still too dark to polarize in the 200-mm tube. In such cases the shorter tube may be used and its reading multiplied by 2, but the zero deviation must then be determined and applied to the product. This will give the reading which would have been obtained if a 200-mm tube could have been used, and it only remains to apply the correction determined by the use of the control plate.

Example

Solution reads in 100-mm tube	47.0	
Multiplied by 2	2.0	
Product	94.0	
Zero reads plus 0.3	.3	
Solution would read in 200-mm tube		93.7
Reading of control plate	90.4	
Sugar value of control plate	90.5	
Scale reading too low by		.1
Add 0.1 to 93.7.		
Correct polarization of solution		93.8

Before filling the tube it must either be thoroughly washed and dried or rinsed several times with a portion of the solution itself. The cover glasses must also be clean and dry and without serious defects or scratches. Under no circumstances, after sufficient liquid has passed through the filter, shall more than 12 minutes elapse before the tube is filled. Unnecessary warming of the tube by the hands during the filling must be avoided. It is closed at one end with the screw cap and cover glass and grasped by the other end with the thumb and finger. The solution shall then be poured in until the tube is nearly filled, leaving space for an air bubble when the cover glass is in place. The air bubble shall be as large as possible without being visible when the tube is held in a horizontal position. Care shall be taken that the outside portion of the cover glasses remain clean and dried. If this result is not attained, the operation shall be repeated, the cover glass being washed clean and dry and the solution again brought up over the end by adding a few more drops. The cover glass being in position, the tube shall be closed by screwing on the cap. The greatest care must be observed in screwing down the caps that they do not press too tightly upon the cover glasses. By such pressure the glasses themselves may become optically active and cause erroneous readings when placed in the instrument. It shall therefore be ascertained or made sure that the rubber washers are in position over the cover glasses and the caps shall be screwed on lightly. A cover glass that has once been compressed may part with its acquired optical activity very slowly and not less than 7 official days shall be allowed to elapse before it is used again.

Polarizing sugar.—Before the polariscopic reading on the polariscope tube shall be taken, an observation on the quartz control plate shall be made. The tube must be read without altering the position of the instrument relative to the light or changing the character of the light in any way. When a series of successive polarizations is made under the same conditions as regards temperature, position of the instrument with relation to the light, intensity of the light, etc., the observation on the control plate need not be made before each polarization; one such observation shall be sufficient for the entire series. The control observation must be repeated oftener if the observer has the slightest reason to think that any of the factors just indicated have been altered. After the polariscope tube has been placed in the polariscope, the observing telescope shall be so adjusted as to bring the dividing line between the two halves of the field into sharp focus and at the same time cause it to vanish as nearly as possible. This condition must be carefully fulfilled before any observation is taken. Each polariscope tube shall be read on two different instruments by the same observer, and not less than three careful readings of the tube shall be made on each instrument. After the average of these three readings has been corrected by means of the quartz control plate, it shall be taken as the polarization of the tube on that polariscope. The average of the two averages obtained from the two polariscopes shall be taken as the final polarization of the tube.

Determination of sucrose in cane sirups and molasses.—The method for the determination of sucrose in cane sirups and molasses shall be as follows: Prepare a solution of the molasses containing 65 g in 500 ml (half-normal), 26 g in 250 ml (two-fifths normal), or 13 g in 250 ml (one-fifth normal), according to the nature of the substance. Make to volume at the temperature at which the polariscopic observations are to be made, clarify with the minimum quantity of Horne's dry basic lead acetate, and shake thoroughly. Filter.

Pipette two 75-ml portions of the clear filtrate into two 100-ml volumetric flasks.

Direct polarization.—To 1 portion add 10 ml of a solution of sodium chloride containing 231.5 g per liter. Make to volume at the temperature at which the polariscopic observations are to be made. Shake and filter as rapidly as possible in order to avoid resolution of lead chloride. Polarize.

Invert polarization.—To the other portion add 10 ml of hydrochloric acid (d 20°/4°, 1.1029). Immerse in a water bath which is maintained at 60° C. Agitate the solution continually for 3 minutes and allow it to remain in the bath for a total time of 10 minutes. Cool quickly and make to volume at the temperature at which the observations are to be made. Shake and filter as rapidly as possible. Polarize.

All polarizations shall be made in water-jacketed tubes provided with tubulature and thermometer.

Correct both readings for zero point displacement. Take the algebraic difference between the direct and invert polarizations and convert to 26 g basis by multiplying by 8/3, 10/3, or 20/3, according to the normality of the original solution. This gives the value $P—P'$ to be used in the final calculation.

In order to find the proper Clerget divisor, $P—P'$ is multiplied by the normality fraction of the original solution, i. e., 1/2, 2/5, or 4/5. From table 19, National Bureau of Standards Scientific Paper S375, page 189, under the column marked "75 ml × 4/3" and opposite the value of $P—P'$ (reduced by the normality fraction), find the value of the Clerget divisor. Apply the temperature correction and divide into $P—P'$[1].

The pipetting of solutions shall be done with great care. The pipettes must be kept scrupulously clean by frequent use of a bichromate sulfuric acid cleaning mixture, the lead being first removed with alkaline tartrate solution. During delivery it shall be held in a vertical position and allowed to drain by gravity for the definite length of time specified by the calibration.

It is advisable to perform the direct and invert polarizations for each analysis during the same series of observations, placing the tubes side by side and feeding the water jackets from the same source.

The hydrochloric acid (d 20°/4°, 1.1029) is made by diluting the concentrated cp acid by approximately an equal volume of water. It is sufficiently accurate to adjust the diluted solution to a density of 24.9 Brix at 20.0° C.

Determination of reducing sugars in cane sirups and molasses.—The method for the determination of the reducing sugars in cane sirups and molasses containing approximately 50 percent total sugars shall be as follows: Eight grams of molasses are transferred to a 500-ml flask, dissolved, clarified with a minimum quantity of normal lead acetate solution and made to volume and filtered. The filtrate is freed from excess of lead by the addition of dry potassium oxalate. Aliquot portions of 50 ml of the lead-free filtrate are taken for analysis. Transfer 25 ml each of solutions A and B of the Soxhlet reagent to a 400-ml beaker and add 50 ml of the above solution. Heat the beaker upon an asbestos gauze over a Bunsen burner, so regulating the flame that boiling begins in 4 minutes and continues boiling for exactly 2 minutes. Keep the beaker covered with a watch glass throughout the entire time of heating. Without diluting, filter the cuprous oxide at once on a Gooch crucible, using suction. Wash the cuprous oxide thoroughly with water at a temperature of about 60° C, then with 10 ml of alcohol, and dry for 15 minutes in an oven at 100° C. Ignite crucible for 10 minutes over a Bunsen burner. The precipitate is reduced to metallic copper in methyl alcohol vapors. This is done by placing about 15 ml of methyl alcohol in a 400 ml beaker, placing a triangle support in the beaker so the top is above the level of the alcohol. Heat covered beaker to boiling on hot plate; remove cover and place hot Gooch crucible on triangle. This ignites the alcohol vapors. Immediately cover with watch glass and allow to remain for about 6 minutes, remove, dry in an oven at 100° C for about 5 minutes, cool in desiccator, and weigh. The amount of reducing sugar corresponding to this weight of copper is found from table 78, p. 564 (column marked "0.4 g total sugar").

Control determinations should be carried out, using standard dextrose. In the event that the percentage of total sugars in the molasses varies appreciably from 50 percent, such a weight is taken for the reducing-sugar determination, that 50 ml of the solution will contain 0.4 or 0.3 g total sugar to conform to the specifications of the method of Munson and Walker.

Example.—In a sirup containing 80 percent of total sugars, 5 g of the sample are dissolved and made up to 500 ml, and 50-ml portions taken for analysis, each such portion containing 0.5 g of sample or 0.4 g of total sugars.

Determination of sucrose and raffinose in beet molasses.—The method for the determination of the sucrose and raffinose in beet molasses shall be as follows: Prepare a solution of the beet molasses containing 65 g in 500 ml (half normal). Make to volume at the temperature at which the polariscopic observations are to be made. Clarify with the minimum quantity of Horne's dry basic lead acetate and shake thoroughly. Filter.

Direct polarization.—Polarize the solution to obtain the direct reading and correct first for zero point displacement and then correct to the value which would have been obtained if 26 g of the sample were taken in 100 ml of solution, (P).

Invert polarization.—Pipette 75 ml of the clear filtrate into a 100-ml flask, add 10 ml of HCl (d 20°/4°, 1.1029). Immerse in a water bath which is maintained at 70° C. Agitate continually for 3 minutes and allow to remain in the bath for a total time of 10 minutes. Cool quickly and make up to volume at the temperature at which the observations are to be made. Shake and filter as rapidly as possible. Polarize. Correct first for zero-point displacement, and then correct to the value which would have been obtained if 26 g of the sample were taken in 100 ml of solution (P').

[1] See also p. 155.

All polarizations shall be made in water-jacketed tubes provided with tubulature and thermometer.

Substitute these values of P and P' in the following equation:

$$S=\frac{(.5142+.00196(t-20))P-P'}{.8413-.00320(t-20)}. \tag{145}$$

Substitute the value of S and the value of P in eq. 146 and solve to find the percentage of raffinose:

$$\left.\begin{aligned} R&=\frac{P-(1-.0003(t-20))S}{1.852} \\ \text{or}\quad R&=0.54(P-(1-.003(t-20))S) \end{aligned}\right\} \tag{146}$$

Determination of reducing sugars in beet molasses.—The method for the determination of reducing sugars in beet molasses shall be as follows:

For the determination of reducing sugars in a molasses containing approximately 50 percent of total sugars, 20 g of the beet molasses are transferred to a 250-ml flask, dissolved, clarified with the minimum quantity of normal lead acetate, made to volume, and filtered. The clear filtrate is freed from the excess of lead with dry potassium oxalate. Taking aliquot portions of 50 ml of the lead-free filtrate, the reducing sugars are determined as described under "cane molasses." Find the amount of reducing sugars corresponding to the weight of copper obtained from table 78, p. 564 (column marked "2 g total sugars").

In the event that the percentage of total sugars in the beet molasses varies appreciably from 50 percent, such a weight is taken that 50 ml of the solution will contain 2 g of total sugars.

Determination of weight per gallon of molasses.[49]—A special 100-ml volumetric flask with a neck of approximately 8-mm inside diameter shall be used. Weigh the flask empty and then fill it with molasses, using a long-stemmed funnel reaching below the graduation mark, until the level of the molasses is up to the lower end of the neck of the flask. The flow of molasses may be stopped by inserting a glass rod of suitable size into the funnel so as to close the stem opening. Remove the funnel carefully to prevent molasses coming in contact with the neck, and weigh flask and molasses. Add water almost up to the graduation mark, running the water down the side of the neck to prevent mixing with the molasses. Allow to stand for several hours or overnight to permit the escape of bubbles. Place the flask in a constant-temperature water bath, preferably at 20° C, for a sufficient time for it to reach the temperature of the bath, then make to volume at that temperature, with water. Weigh. Reduce the weight of the molasses to vacuo and calculate the density. From table 117, page 644, convert to weight per gallon in air.

Correction for temperature.—The temperature of the molasses shall be determined at the time of gauging. The weight per gallon of the molasses shall be corrected to this temperature, using as the factor for the cubical expansion of molasses 0.00043 per unit volume per degree centigrade. The weight per gallon at the temperature of gauging is therefore

$$W_2=\frac{W_1}{1+0.00043(t_2-t_1)}, \tag{147}$$

where

t_1=temperature of determination,
t_2=temperature of gauging,
W_2=weight per gallon at temperature, t_2,
W_1=weight per gallon at temperature, t_1.

Moisture determination.—For the determination of moisture in sugars, dry approximately 4 g in a metal dish of a diameter of 55 mm and a height of 15 mm. Each sample shall be subjected to a temperature of 100° C for 2 hours, care being exercised that the dishes are not in close proximity to the heaters.

[49] An example of the calculation is given on page 252 of this Circular.

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